Chemical Monographs

The Chemistry of Combustion

J. NEWTON FRIEND

Gurney and Jackson

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CHEMICAL MONOGRAPHS

EDITED BY A. C. CUMMING, O.B.E., D.Sc., F.I.C.

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THE progress of Chemistry is so rapid that it is becoming a matter of ever-increasing difficulty to keep abreast of the modern developments of the science. The volume of periodical literature is so enormous that few can hope to read, far less assimilate, all that is published. The preparation of summaries has therefore become a necessity, and has led to the publication of various well-known journals devoted to the abstraction of original papers. For obvious reasons, however, these do not fully supply the wants of advanced students and research workers, and it is now generally recognised that monographs on special subjects are also needed.

This series of monographs is intended primarily for Advanced and Honours students. As each monograph is written by an author with special knowledge of the subject, and copious references are given, it is hoped that the series will prove useful also to those engaged in research.

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The Chemistry of Combustion

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PREFACE

THIS little book is the outcome of a series of lectures delivered to my senior students in the Chemical Department of the Birmingham Municipal Technical School during the Session 1920 to 1921. There appeared to be no small Text-book or Monograph to which the students could be referred dealing with the subject in its more modern aspect, and it was felt that the publication of my lectures might serve to fill, however imperfectly, a very obvious gap in our literature.

My sincerest thanks are due to Dr A. Parker, who has carefully read through the proof sheets and made many valuable suggestions. I am glad also to take this opportunity of thanking Miss Annie R. Russell, B.Sc., of this School, for assistance and advice.

J. NEWTON FRIEND.

November 1921.

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THE CHEMISTRY OF COMBUSTION

SECTION I.

Definitions.

An old Spanish proverb states that "Where there is no hook to be sure there will hang no bacon." With equal truth it might be said that *where there are no definitions to be sure there can be no science.* For science is organised knowledge, and unless our terms are carefully defined our dissertations will inevitably be diffuse and obscure, if not indeed actually misleading.

In no field of science is the need for a clear conception of the meaning of certain terms more necessary than in that now under discussion. The knowledge that certain substances will burn must be almost as ancient as man himself. Such terms as fire, flame, and combustion have for centuries been household expressions, and as such they have been frequently used to denote phenomena, which to the popular mind may appear like, but which in reality are widely separated from each other. In a critical discussion, therefore, of the various phases of combustion, it becomes necessary, if the

introduction of a large number of new terms is to be avoided, to give at the outset precise meanings to such popular terms as it is desired to employ.

By **combustion** it is now usual to imply some form of chemical change accompanied by the evolution of both heat and light. Thus, for example, the raising of platinum wire to redness through the agency of an electric current and the production of beautiful optical phenomena by passing electrical discharges through Geissler tubes are not examples of combustion, for although both heat and light are emitted, they are not accompanied by chemical change. On the other hand, combustion takes place when phosphorus burns in oxygen, for the enormous heat and dazzling light are accompanied by vigorous chemical change.

Although in the large majority of cases combustion is the result of oxidation, it would be erroneous to suppose that combustion cannot also take place in the entire absence of oxygen whether free or combined. Thus if a small jet of burning coal-gas [1a] is plunged into a jar of chlorine, combustion continues, although a marked change takes place in the attendant phenomena. The flame becomes deep orange in colour, and volumes of black soot are evolved; the yellowish-green colour of the chlorine gradually disappears, giving place to steamy clouds of hydrochloric acid gas. A familiar lecture experiment is to plunge yellow phosphorus into bromine vapour when it readily burns yielding clouds of mixed bromides, whilst powdered arsenic dropped upon liquid bromine immediately inflames. A piece

of copper foil burns brilliantly in sulphur vapour, and a rod of iron heated to redness and pressed against a piece of sulphur behaves similarly in the vapour thus produced, the molten ferrous sulphide falling in scintillating globules to the ground.

These are, all of them, examples of true combustion, but of combustion in the entire absence of oxygen. As mentioned above, however, in the vast majority of cases combustion is accompanied by oxidation, mainly in consequence of the fact that the chemically active constituent of the atmosphere is oxygen. Had our atmosphere consisted of chlorine we should still have been familiar with combustion, but most examples would have been the result of chlorination.

One of the chief factors which determines whether or not chemical change shall be accompanied by combustion is the magnitude of the heat evolution. On applying a light to a jet of hydrogen issuing from a tube into the air, the hydrogen readily burns, and if the surrounding air be replaced by oxygen, the temperature of the reaction rises rapidly, an intense heat being produced.

The reaction is thus powerfully exothermic, the amount of heat evolved being as follows:—

$$(H_2) + (O) = (H_2O) + 58{,}700 \text{ calories}$$

at room temperature. The physical state of the reacting masses is indicated by the brackets. Rounded brackets mean that the substances are present in the gaseous state; square brackets [ ] indicate the solid state, whilst an entire absence of brackets indicates the liquid state.

The above equation tells us that gaseous hydrogen and oxygen unite to form water vapour, and that for every gram-molecule of hydrogen burned or of water produced 58,700 gram-calories of heat are evolved.

If the water vapour is allowed to condense to liquid water, allowance must be made for the change of state involved which causes the evolution of still more heat—the latent heat of steam. This must be added to the previous amount and our equation now becomes [1]

$$(H_2)+(O) = H_2O + 68{,}360 \text{ calories.}$$

The molecule of water is not bracketed as it is now assumed to be in the liquid state.

But when hydrogen combines with oxygen, combustion does not always ensue. This has been known for many years. Hooke in 1803 observed that electrolytic gas confined in vessels over water very slowly combined at the room temperature,[2] the amount of combination being appreciable only after several months. As the temperature is raised, the rate of combination steadily increases [3] and proceeds with a measurable velocity at about 450° C.[4] There is still no sign of combustion, however, in the sense in which the term has been defined above, so that evidently the mere fact that a reaction is powerfully exothermic is not in itself sufficient guarantee that it shall be accompanied by combustion. The conditions obtaining at the time of experimentation must also be considered.

It is immaterial in regard to the quantitative heat

evolution whether one element combines rapidly with another, or slowly. The same amount of heat per gram-molecule is evolved in either case, provided the initial and final phases are identical in the two sets of experiments. If the reaction proceeds very slowly the heat set free will ordinarily be dissipated with such relative rapidity that no sensible rise in temperature occurs, and the reaction may even proceed to completion without the phenomena characteristic of combustion ever appearing.

From the foregoing it will be clear that exothermic chemical reactions may take place with all degrees of velocity, ranging from that which proceeds so slowly as to be measurable only after many months up to that which is practically instantaneous or explosive. When a reaction occurs with a sensible rise in temperature, but unaccompanied by light, it is frequently termed **slow combustion.** The oxidation of impurities in the blood by air drawn into the lungs is a familiar example. In the majority of these cases the reaction does actually proceed slowly, and the term is unexceptionable. But such is not always the case. Every student of chemistry knows that nitric oxide, itself a colourless gas, is characterised by the readiness with which it combines with oxygen to yield rich brown fumes of nitrogen peroxide. The reaction is markedly exothermic, the heat evolution being as follows :—

$$2(NO) + (O_2) = (N_2O_4) + 40{,}500 \text{ calories},$$

and if suitable precautions are taken, a rise in temperature can readily be observed. This is an

example of "slow" combustion, as defined above, although the reaction is not in itself a "slow" one. Bearing in mind, however, the extended use of the prefix in this connection, the term slow combustion is a very convenient one to retain.

Although most substances require to be raised in temperature before combustion can ensue, a number of reactions are known in which the ingredients react vigorously with evolution of light and heat practically from the moment they are brought into contact with one another. Such reactions are examples of **spontaneous combustion.** Thus sulphur spontaneously burns in fluorine even at $-187°$ C. forming the hexafluoride SF_6. At ordinary temperatures both ammonia and nitric oxide inflame when brought into contact with fluorine, yellow phosphorus readily catches fire in chlorine, and powdered arsenic instantly inflames on the surface of liquid bromine. The pyrophoric metals become incandescent in moist air, whilst liquid phosphine, silico-ethane, and many organic substances immediately ignite in contact with oxygen or air.

The temperature at which rapid combustion becomes independent of external supplies of heat is known as the **ignition temperature.**

A mass of gas raised to incandescence by heat is termed a **flame**; this latter is produced only in those cases of combustion in which gases or vapours are present. Flame, however, does not always accompany rapid gaseous combustion, a striking exception being afforded by the rapid oxidation of hydrogen or coal-gas mixed with air on a catalysing surface,

such as that of platinised asbestos or porous firebrick. Such combustion is termed **flameless** or **surface combustion**, and is utilised commercially in a variety of ways.

A substance undergoing slow combustion may exhibit pronounced luminosity or **phosphorescence.** This is not an exceptional phenomenon, as was formerly believed, but a natural prelude to rapid combustion, the appearance of flame being the culminating point of a series of changes, and coincident with the ignition temperature.[5] Many substances are now known to exhibit phosphorescence, but the temperature of its appearance is so high or the temperature interval during which the phenomenon is perceptible is frequently so short as to be ordinarily overlooked. In the case of phosphorus it is particularly well marked, the temperature intervals, namely, 7° to 60° C., including the ordinary range of atmospheric temperature, so that the phosphorescence could hardly be overlooked. Had an arctic climate prevailed, however, the phosphorescence would not have been so readily observed, for in igniting phosphorus with a match or taper the phosphorescent temperature interval would be rapidly passed, as is the case under existing conditions with sulphur. Occasionally phosphorescence is referred to as *degraded combustion.* This is not a happy term, however, suggesting as it does that combustion is not complete. This may often be the case, but it is not universally so, sulphur being a case in point. This element phosphoresces direct to the dioxide, no incomplete oxidation products being obtained.[5]

When a reaction proceeds with a rise of temperature and an ever-increasing velocity until a high maximum velocity is attained, an **explosion** or **detonation** results.

Combustion is greatly facilitated by fineness of division. This is well illustrated by the pyrophoric metals. If yellow phosphorus is dissolved in carbon disulphide and the solution poured over some filter paper, the solvent rapidly evaporates leaving the phosphorus in a very fine state of subdivision, and inflammation rapidly takes place.

Many explosions in factories, mines, etc., have been definitely traced to the presence of dust, the activity of which is largely a surface phenomenon akin to those now under discussion. The influence of dust may be illustrated in a harmless manner by introducing some very finely powdered coal or charcoal into a gas jar to the depth of about half an inch, and blowing oxygen into it from a glass tube reaching to the bottom. When the oxygen-enriched air in the jar is thick with dust, a light is applied with a long taper, and a flame flashes down the jar with explosive violence.

SECTION II.

Phlogiston.[1]

For many centuries prior to the discovery of oxygen it had been assumed that all combustible bodies possessed a combustible principle—the *fire matter* of the Greek philosophers. Owing to its ready combustibility, sulphur was for long regarded by European alchemists as the essential principle of combustion. Becher (1635-1682) christened this principle *terra pinguis* or "oily earth," and distinguished it from sulphur which, however, he regarded as rich in this principle. When a substance burned, therefore, the oily matter escaped leaving an incombustible ash or **calx** (from the Latin *calx*, lime). Stahl (1660-1734) developed Becher's views, modified and extended them. He termed the combustible principle **phlogiston** from the Greek φλογίξειν, to ignite. When, therefore, a metal such as zinc burned in air, phlogiston escaped, the residual ash of dephlogisticated metal being termed zinc calx. Thus,

$$\text{zinc} = \text{zinc calx} + \text{phlogiston}.$$

The residual air (nitrogen), now saturated with phlogiston was termed *phlogisticated air*. Stahl appears to have regarded carbon as almost pure

phlogiston, and other chemists subsequently viewed hydrogen in the same light.

So long as the adherents of the phlogistic theory were content to regard phlogiston as a principle only, and not as a material body, the theory was distinctly attractive, phlogiston being the prototype of what we now term the **heat tone** or **heat of reaction.** Such a theory, however, could not offer a complete explanation for many of the phenomena known, even in the times of Becher and Stahl, to be attendant upon combustion, but the materialisation of phlogiston, whilst removing some difficulties, introduced many others. Thus, for example, the identification of phlogiston with hydrogen enabled chemists to correlate the escape of this gas upon the solution of metals in acids with the combustion of the same metals in air; at the same time it introduced the very serious difficulty that no hydrogen could actually be detected in the air after the combustion of a metal, and no answer was forthcoming as to whither it had escaped.[2]

The two chief difficulties which ultimately led to the overthrow of the phlogistic theory were the following:—

1. It had been known for many centuries that ordinary combustion would not take place in the absence of air. Thus the Arab chemist Geber, in the eighth century, stated that the calcination of mercury must be carried out in open vessels, and Stahl himself was aware that even soot, which he regarded as almost pure phlogiston, would not burn out of contact with air. This was explained on the

assumption that the phlogiston could not leave a substance unless it had somewhere to go to. In other words, the air was believed to act as an absorbent for the phlogiston just as a sponge sucks up water or as charcoal adsorbs colouring matter from liquids and bad odours from gases. This ingenious explanation, however, takes no cognisance of the fact that the volume of the air actually becomes smaller during the calcination of metals.

2. In 1630, Jean Rey had drawn attention to the fact that both lead and tin exhibit an *increase in weight* upon calcination in air. Now, according to the phlogistic theory,

$$\text{metal} = \text{calx} + \text{phlogiston},$$

so that even if phlogiston was a non-material and imponderable principle, the metal could not weigh less than the calx; whilst if phlogiston was materialised into carbon, hydrogen, or any other substance, the metal must weigh proportionately more than its calx. This anomaly was realised by several chemists; but mere recognition of a difficulty does not involve its solution, and it was not until the discovery of oxygen by the Birmingham divine, Priestley,[3] that Lavoisier was able to offer a more correct theory of calcination and aerial combustion. According to him, when a substance burns in air it combines with the oxygen to form an oxide—an explanation that is regarded as correct at the present time.

SECTION III.

The Combustion of Solid Carbon.

It is a matter of common knowledge that when carbon is allowed to burn in excess of air or oxygen the only product is carbon dioxide; whereas, if the supply of air is restricted, carbon monoxide appears in amounts varying according to the conditions. This is capable of explanation in one of three ways, namely:—

1. It may be assumed that the first product of the interaction of carbon and oxygen is the dioxide, CO_2, and that this, in contact with excess of carbon, is reduced to the monoxide, CO. Thus:—

$$(1)\quad C + O_2 = CO_2$$
$$(2)\quad CO_2 + C = 2CO.$$

After the overthrow of the phlogistic theory, and during the major part of last century, this was the commonly accepted theory.[1]

2. In 1872 Sir Lowthian Bell, as the result of long continued study of the chemical processes involved in iron smelting, concluded that "carbon monoxide and not carbon dioxide is the chief, if not the exclusive and immediate action of the hot blast on the fuel" (coke).

According to this the presence of carbon dioxide is due to oxidation of the monoxide in excess of air, the gas thus being a secondary instead of a primary product. Thus:—

$$(1)\quad 2C + O_2 = 2CO$$
$$(2)\quad 2CO + O_2 = 2CO_2.$$

This second theory received support from a number of interesting observations. Thus in 1887, C. J. Baker[2] observed that carbon, which has been thoroughly dried by exposure to phosphorus pentoxide, is allowed to absorb oxygen, dried in a similar manner at 12° C. and is then heated to 450° C.; the evolved gas consists mainly of carbon monoxide. Having satisfied himself that, under the conditions of his experiments, carbon dioxide if initially formed could not have been reduced to the monoxide, Baker concluded that carbon is oxidised directly to carbon monoxide by the absorbed oxygen.

These conclusions were supported the following year by H. B. Baker[3] who showed that:—

(i.) Thoroughly dry carbon dioxide is not reduced by dry carbon even at bright red heat.

(ii.) Carbon monoxide is the main product of the combustion of carbon in dry oxygen.

Thus, when oxygen which had been thoroughly dried by prolonged contact with phosphorus pentoxide was passed over highly purified sugar charcoal at bright red heat, no visible combustion occurred.

The gases passing over possessed the following composition :—

Oxygen	58·1 per cent.
Carbon monoxide . .	39·5 „
Carbon dioxide . . .	2·2 „

Bell's theory thus appeared to be well substantiated.

3. In 1913, however, a new complexion was put upon the whole problem by the extensive researches of Rhead and Wheeler.[4] These investigators found that charcoal which has been heated in a vacuum up to 950° C. and allowed to cool, readily absorbs or occludes appreciable quantities of oxygen at all lower temperatures. The amount of occluded oxygen increases with fall of temperature, and remains surprisingly constant for any given temperature for the particular specimen of charcoal employed.

The rate of absorption of oxygen by exhausted charcoal is exceedingly rapid during the first fifteen seconds, after which a slow absorption continues over several hours. This is well illustrated in Fig. 1, which depicts the relative amounts of oxygen absorbed at various temperatures during short intervals of time. The type of curve is seen to be the same for each temperature, the main differences consisting not in the rates of fixation of the oxygen, but in the respective quantities of the gas.

This rather suggests that the absorption is a purely physical phenomenon. On the other hand, it is found that the oxygen clings so tenaciously to the carbon as to defy removal by the most complete exhaustion at any given temperature, provided that temperature

remains constant. If the temperature is raised by a certain amount, a definite quantity of oxygen is removed *in vacuo* in the form of a mixture of carbon monoxide and dioxide until the saturation point of the charcoal at this new temperature is reached, after

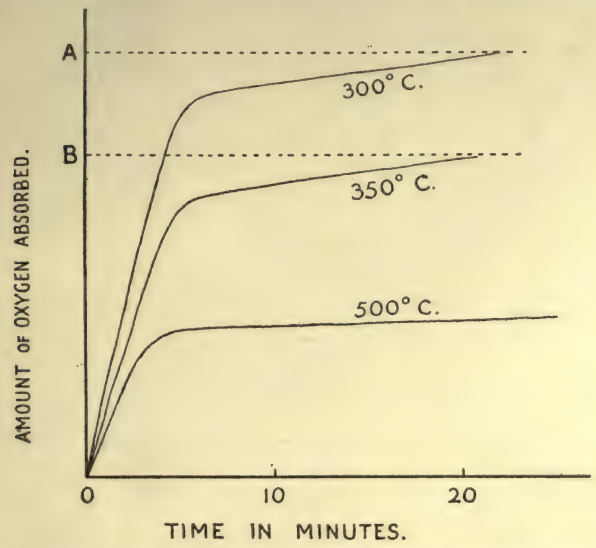


FIG. 1.—Absorption of Oxygen by exhausted Charcoal (*Rhead and Wheeler*).

which no further gas is removable without another rise in temperature.

Thus, if the temperature were raised from 300° C. to 350° C. the amount of oxygen liberated *in vacuo* as oxides of carbon would correspond to the fall in concentration in the charcoal from A to B.

If this is a case of purely physical absorption it

is surprising that a reduction in pressure should alone be insufficient to remove either oxygen or its oxidation products, the monoxide and dioxide of carbon, at temperatures below 900° C.[5] Again, one would have expected that admission of either of the oxides of carbon to exhausted carbon at temperatures sufficiently low to avoid chemical action, for example, 250° C., would result in a partial absorption of some of them. This, however, has been demonstrated not to be the case.

Rhead and Wheeler therefore conclude that the first product of the combustion of carbon is a loosely formed complex which may be regarded as an unstable compound of carbon and oxygen of an unknown formula, C_xO_y. This is presumed to be formed by the "fixation" of such oxygen molecules as come into collision with the carbon. There are good grounds for believing that the carbon molecule is extremely complex in structure,[6] and the authors suggest that during oxidation the oxygen molecule may actually penetrate into the carbon molecule, a rearrangement of the atoms taking place. However this may be, it is sufficient to assume that the oxygen molecule is temporarily fixed. The repeated fixation of oxygen molecules, however, causes the evolution of a considerable amount of heat, so that some of the molecules eventually acquire sufficient energy to seize hold of a carbon atom and depart with it as carbon dioxide. Some of them become torn apart in the process and leave the carbon molecule as carbon monoxide.

The formation and partial decomposition of the

intermediate compound, C_xO_y, continues until the carbon becomes "saturated" with oxygen, after which there is alternate formation and decomposition of the complex. Each oxygen molecule that impinges on the carbon liberates so much energy upon fixation that the equivalent amount of monoxide or dioxide is liberated by disruption of a certain quantity of C_xO_y formed from previous oxygen molecules.

This attractive theory, whilst not definitely proven, appears to fit in extremely well with known facts, and is not at variance with any of the arguments brought forward in support of either of the two previous theories.

Composition of the Complex, C_xO_y.—The quantity of oxygen absorbed by a sample of charcoal at 300° C. in one experiment amounted to 0·16 gram per 12 grams of the latter, so that the empirical composition of the complex would be represented by the formula, $C_{100}O$.

On the other hand, the relative proportions of carbon dioxide and monoxide evolved on raising the temperature of saturated charcoal is found to vary with the initial temperature, so that it would appear impossible[7] from available data to determine the actual values for x and y.

Combustion in a Coke-fired Furnace.

When a current of ordinary air is injected into a furnace on to a mass of incandescent carbon (coke), the complex C_xO_y initially formed is rapidly decomposed yielding a mixture of the two oxides of carbon.

These tend, also rapidly, to reach a condition of equilibrium as represented by the equation

$$2CO \rightleftharpoons C + CO_2.$$

Accordingly, if the time required to attain to this equilibrium at high temperatures is less than that taken by the gaseous phase to traverse the fuel bed, given constant pressure and temperature, the ratio CO_2/CO, as found in the emergent gases, should remain constant.

If the coke is at a high temperature, namely, not less than 1200° C., then approximately 99·94 per cent. of the gaseous mixture consists of carbon monoxide, and the reaction may be considered as taking place according to the equation

$$2C + O_2 = 2CO + 58{,}000 \text{ calories},$$

although, theoretically, no matter how high the temperature attained, a small but definite proportion of carbon dioxide must always be present to maintain equilibrium.

SECTION IV.

Flame.

A FLAME has already been defined as a mass of gas raised to incandescence by heat. According to this definition it is possible for us to have flame without combustion, and this may be experimentally realised during the passage of electricity through rarefied gases. Such is the exception and not the rule, however, and our concern is with those flames that are a manifestation of combustion.

Perhaps the most satisfactory method of studying flames is to take a few typical examples and examine them in detail.

The Candle Flame.

The candle flame is a never-failing source of interest. The fuel is solid, but is gradually liquefied by the heat generated when once combustion has been started, and lies in a cup-shaped hollow at the foot of the wick. By capillary attraction some of this molten fuel is continually being drawn up the wick, and, reaching a much hotter zone, is not only vaporised but ignited. If the candle flame is blown out, and the whitish vapours of paraffin escaping from the wick are brought immediately

into contact with a lighted taper (and thus not given time to cool and condense), a flame from the latter instantly darts across the intervening space to the wick, and the candle relights.

The flame consists of gases which, at the temperature prevailing, are lighter than the surrounding air, so that the flame rises. This is a fortunate

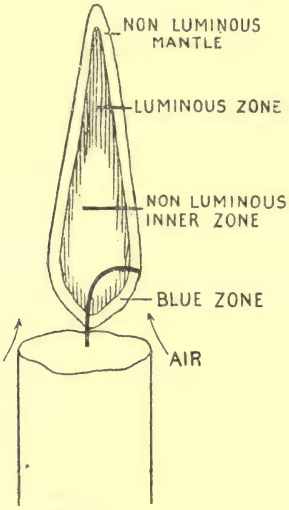


Fig. 2.

circumstance, although in a sense it is purely an accident. One result is that as the flame burns, cool air is drawn up from below, as shown in Fig. 2, and keeps the outer edge of the wax cool. It thus enables the molten fuel to lie in a cup-shaped receptacle of solid fuel without overflowing, as already mentioned. If the wick is not central, or if the candle is not cylindrical, or finally, if the flame is

exposed to a draught, this balance is disturbed and may result in molten wax overflowing and running down the sides where it congeals in characteristic streaks. As a rule, therefore, ornate candles are not as efficient as the plain, cylindrical ones. Examination of the candle flame itself reveals a number of interesting points.[1] It is possible to distinguish four parts in the flame, namely :—

(1) The *inner, non-luminous zone* (see Fig. 2) which consists essentially of vaporised

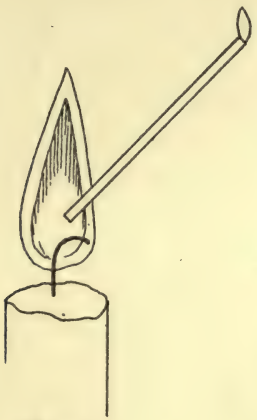


Fig. 3.

paraffin wax. It has not had a chance to burn as yet, for appreciable amounts of air have not penetrated so far. It represents the first stage in the gasification of the wax.

If a narrow glass tube is inserted in the flame as shown in Fig. 3 with its lower end

in the non-luminous zone, whitish gases are seen to ascend the tube and to escape at the top. They closely resemble the vapours obtained when the candle flame is suddenly blown out, and consist of vaporised paraffin mixed with some products of combustion. If the tube is warm and not too long the gases, upon ignition, will continue to burn at the top, affording a replica of the candle flame below.

The temperature near the apex of this zone approaches 1000° C.

(2) Surrounding the inner, non-luminous zone is a luminous portion known as the *luminous mantle* or *zone*. Here the temperature ranges from 1000° to 1300° C. Chemical change has now set in, to be completed in

(3) The *non-luminous outer mantle*, where the carbon and hydrogen are completely oxidised in excess of air to carbon dioxide and water. This is the hottest part of the flame and it is in this mantle that the wick, already partially carbonised, oxidises away completely and thus does not require to be snuffed, as it would do if it went straight up into the main portion of the luminous mantle, where it would interfere with the normal burning of the candle.

(4) A small *blue zone* is usually distinguishable just beneath the wick.

Causes of Luminosity.

The question now arises as to what actually causes the luminosity of the zone immediately within the non-luminous outer mantle of the candle flame.

Before attempting to draw any general conclusion, let us examine a few of the more prominent features of the luminous and non-luminous portions of the flame.

(1) On introducing a cold surface of porcelain into the outer non-luminous mantle no visible change occurs, but if once this mantle is penetrated and the luminous zone allowed to impinge upon the cold porcelain, the latter immediately becomes coated with a deposit of soot. There is thus a distinct difference between the two portions of the flame, the luminous portion behaving exactly as if it contained in suspension small particles of soot or carbon at white heat. On the other hand, a precisely similar deposit would be obtained by the decomposition of heated, dense hydrocarbons under like treatment. Hence this experimental result is capable of a double interpretation.

(2) If a jet of hydrogen issuing from a glass tube is ignited, the flame is at first almost colourless, but as the tube becomes warm the hydrogen flame becomes yellow in consequence of sodium escaping from the glass. If, however, the hydrogen be made to issue

from a platinum tube and to burn in a pure, dust-free air, the flame is invisible and colourless. It may, however, be rendered luminous in at least two ways, namely, either by the introduction of solids, or simply by the purely physical act of increasing the pressure.

The increased luminosity consequent upon introduction of solids into the flame is utilised commercially in the incandescent gas mantles, the introduction of which entirely revolutionised the methods of illuminating private and public buildings.

On the other hand, the fact that mere increase of pressure on the hydrogen flame will increase its luminosity shows that solids are not essential to produce this effect.

(3) When the light from vapours and gases is passed through a spectroscope, a line spectrum is obtained. By increasing the pressure, however, the width of these lines increases, until ultimately a continuous spectrum is obtained, similar to that resulting from an incandescent liquid or solid.

A candle flame likewise shows a continuous spectrum, so that its illuminating constituents must either be solids, liquids, or highly dense vapours.

Conclusion.—It is now evident that the early theory of Davy (1815), namely, that the luminosity of a candle flame is due to the separation and raising

to white heat of solid particles of carbon by incomplete combustion, is not the only explanation that can be offered. For many years Davy's theory was generally accepted, but during the latter half of last century opinion inclined towards Frankland's view (1867) that the luminosity is due to the presence of dense gases[2] produced in the flame as the result of incomplete combustion; and consideration of the above-mentioned observations shows that this theory also is quite in accordance with known facts. It may well be that a complete explanation may include both of these views, and it is by no means impossible that the luminescent substances are in the colloidal state.[2a]

The Coal-Gas Flame.

When coal-gas issuing from a jet is ignited, the resulting flame exhibits the same three prominent zones that characterise the candle flame. A cold porcelain basin becomes covered with soot in the luminous zone, where combustion is partial only, but undergoes no apparent change in the outer mantle. The inner, non-luminous zone consists merely of unburnt gas, and can be abstracted with a small tube precisely as in the case of the candle.

Since the luminous zone owes its light-giving power to the presence of solids or of dense hydrocarbons at a high temperature formed through partial combustion, the question arises as to what would happen if fresh air could be injected straight into this portion of the flame. It is to be expected that combustion would by this means be greatly acceler-

ated and the life-period of any luminous particles rendered so short that the luminosity of the flame would be greatly reduced, if not, indeed, made to disappear entirely.

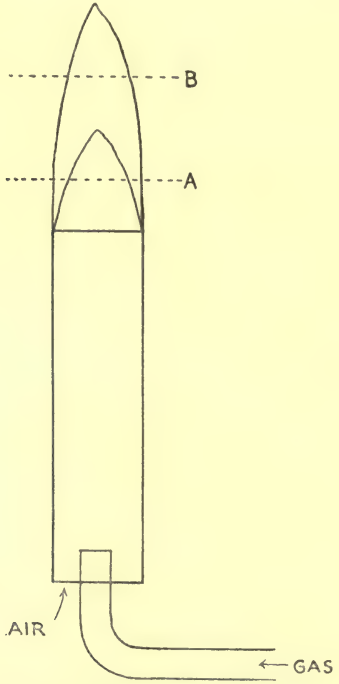


Fig. 4.—A Model Bunsen Burner.

Such in general is the case, as is well illustrated by the Bunsen burner, a useful form of which, for demonstration purposes, consists of a short piece of combustion tubing, some 6 or 8 in. in length, and a piece of narrower tubing bent at right angles and connected with the gas supply (Fig. 4).

A cursory examination of the flame shows that it consists of two parts only, namely, an inner zone of unburnt gas and an outer, also non-luminous mantle in which vigorous combustion is taking place.

The inner portion is cool, so cool that a match head may be thrust into it and kept there unburned, whilst the wooden stem ignites at the junction of the inner and outer zones. A piece of paper held momentarily in a plane at right angles to the mouth of the burner at the level A becomes charred in a ring, the inner portion remaining unaltered. At B, above the apex of the inner zone, the paper is charred in a disc. Similar results are obtained with wire gauze, a red hot ring being formed at A and a red hot disc at B.

The question of the various temperatures attained in a Bunsen flame has been the subject of some little discussion, and published figures show a remarkably wide variation. The data shown in Fig. 5 are probably fairly accurate.[3]

If, whilst the flame is burning, the gas supply be gradually reduced, the flame becomes smaller and smaller, begins to flicker and darts down the tube, and we find an ordinary gas flame now burning at the end of the bent tube. This is called *striking back*. The mixture of air and coal-gas passing up the tube of a Bunsen flame in normal operation is explosive and the flame tends to strike back. Opposing that action is the cooling due to the tube and also the velocity of the mixed gases up the tube. By reducing this latter, however, a point is

reached when the threatened explosion does take place and the flame rushes back—but obviously only so far as the explosive mixture extends, namely to the supply tube.

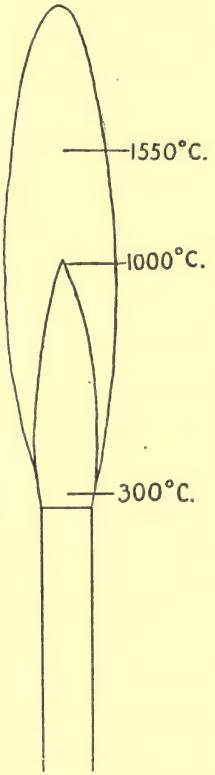


Fig. 5.—The Temperature of the Bunsen Flame.

Smithells' Separator.[4]—By an ingenious arrangement due to Smithells, it is possible to catch the flame in the act of striking back. Two pieces of

combustion tubing are taken, about 8 and 10 in. in length respectively. The longer piece has an external diameter of about 0·2 in. less than the shorter, and is attached to the chimney of a Bunsen burner (Fig. 6).

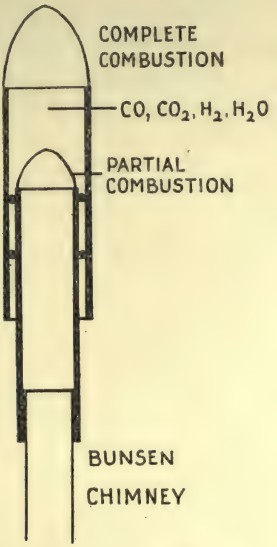


Fig. 6.—Smithells' Separator.

By wrapping a little paper or a rubber ring round the narrower tube the outer one may be loosely attached concentrically. On lighting the gas at the top a normal Bunsen flame is produced. On reducing the pressure of the gas, the flame is seen to flicker as before and part passes down the outer tube until it reaches the inner one, up which the gases are passing with a higher velocity in consequence of its narrower diameter. Here the flame stops. We

have now apparently two flames. In the lower one partial combustion takes place, and a mixture of water, hydrogen, and the oxides of carbon passes to the top where combustion to water and carbon dioxide is completed.

If a piece of wire gauze is gradually brought down on to a Bunsen flame from above, it will be seen that the flame appears to be pressed down, and may even be extinguished if the gauze is brought as low as the top of the chimney. This is because the wire meshwork rapidly conducts the heat away from the flame,

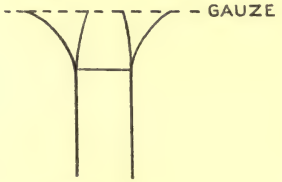


Fig. 7.

cooling the combustible gases on their passage through the gauze to a temperature below their ignition point. If the gauze is held stationary across the flame for a few seconds, it becomes red hot, as we have already seen, and presently the gas above ignites. The heated wires do not now reduce the temperature of the penetrating gases.

If, on the other hand, the wire gauze is laid on the top of the Bunsen chimney, and the gas above it ignited, the gauze may be raised some distance carrying the flame with it. As the heated gases tend to rise and are already above the gauze, the latter keeps cool and there is little tendency for the

flame to travel down. This fact is made use of in the household incandescent burners, some gauze invariably covering the pipe through which the air and gas are supplied, in order to prevent striking back.

This is the principle of the Davy Safety Lamp, for use in mines and other places where the escape of combustible gases renders it dangerous to carry naked lights. Numerous modifications have been introduced from time to time in the lamp, but the principle remains the same. An oil fed wick is surrounded by a glass cylinder, the upper part of which is closed by a cylinder of wire gauze through which fresh air for combustion passes inwards and burned air outwards through the upper portions. Should any marsh gas or fire-damp be present it exerts a peculiar influence on the flame. Small quantities cause a flickering, whilst with larger quantities the flame becomes increasingly elongated. The combustion, however, will not ordinarily pass from the inside of the lamp through the wire gauze, so that the danger of explosions is greatly minimised.

Influence of Pressure on Luminosity.

In 1859 Frankland[2] burned six candles at Chamounix and found a loss in weight of 9·4 grams per candle per hour. The same candles were burned on the summit of Mount Blanc and were found to lose 9·2 grams on the average. Hence the difference in pressure had not materially affected the rate of combustion. Frankland observed, however, that the

inner, non-luminous zone of the flame on the mountain top was larger than in the valley and the luminosity appreciably less. On returning to England he carried out a series of photometric measurements on the influence of pressure on the luminosity of a candle flame, and was able to deduce the following law:—

The diminution of illuminating power is directly proportional to the diminution of atmospheric pressure.

For every fall of 1 in. of the mercury barometer, the luminosity falls by 5·1 per cent. Hence, taking that at London as the standard, namely 100, at München it would be 91, and at Mexico 61·5.

Frankland next showed that the law was trustworthy even up to a pressure of three atmospheres, but at still higher pressures the luminosity rapidly increased, an observation attributable to less complete combustion. His results were as follows:—

Pressure in Atmospheres.	Observed Luminosity.	Calculated Luminosity.
1	100	100
2	263·7	253
3	406	406
4	959	559

Even an alcohol flame becomes very luminous under a pressure of four atmospheres.

Influence of Temperature on Luminosity.

As a general rule, increase of temperature causes a simultaneous increase in the luminosity. If a flame is cooled by bringing near to it a block of cold metal, a distinct reduction in luminosity may be made apparent. On the other hand, by warming coal-gas as it passes through the chimney of a Bunsen burner, the normally non-luminous flame may be made decidedly luminous.

Causes of the Decreased Luminosity of the Bunsen Flame.

The question now arises as to why the Bunsen flame should be non-luminous. This arises from several causes.[5]

First, the injection of oxygen into the heart of the flame causes the rapid, complete combustion of the coal-gas as already indicated. This, however, is only part of the explanation.

Second, the dilution of the flame with atmospheric nitrogen tends to prevent the formation of intermediate luminous products by increasing the temperature necessary to bring about the necessary partial decomposition of the hydrocarbons.

Third, the air introduced into the flame is cold, and thus tends to reduce the effective heating influence brought about by the oxidation consequent upon the admission of atmospheric oxygen.

Reciprocal Combustion.

It must not be overlooked that a flame such as we have been considering is simply a boundary between the combustible gases where chemical combination is proceeding rapidly. It is usual to regard

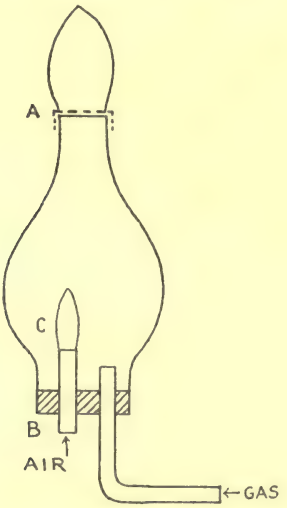


Fig. 8.—Coal-Gas burning in Air, and Air burning in Coal-Gas.

coal-gas as combustible, but this is simply a matter of convenience, for coal-gas is not combustible in so far as nitrogen is concerned, and oxygen is combustible where coal-gas is concerned. That a flame of coal-gas burning in air is simply the inverse of air burning in coal-gas may be very effectively shown by the experiment illustrated in Fig. 8.

The coal-gas supply is turned on full and ignited

at the top of the lamp glass, which may be protected by wire gauze at A to prevent cracking. The gas is turned down slightly to create a draught up B and a lighted taper is carefully passed up. A flame appears at C as soon as the gas is reached—air burning in coal-gas.[6]

SECTION V.

The Combustion of Gaseous Hydrocarbons and Other Gases.

The problems connected with the combustion of gaseous hydrocarbons have been the subject of considerable controversy. During the greater part of last century the theory of **preferential combustion** was widely accepted, according to which there is competition between the different constituents of the burning gases for the oxygen of the air. If, therefore, a hydrocarbon gas undergoes partial combustion in a limited supply of air, the "most favoured" element will tend to burn first, leaving the remainder to oxidise as best it may. In this way the luminosity of a hydrocarbon flame, such as that of ethylene or acetylene, received explanation.[1] The gas is first decomposed into hydrogen and carbon at the high temperature of the flame. The hydrogen being under these conditions the favoured element rapidly burns to steam, whilst the less favoured carbon remains suspended in the flame in a white hot condition, thereby rendering it luminous. Ultimately the carbon itself burns, and the process of combustion is thus completed.

On the other hand Dalton [2] had found, in the early years of last century, that marsh gas, exploded with its own volume of oxygen, yields equal volumes of steam, carbon monoxide, and hydrogen. Thus:

$$CH_4 + O_2 = CO + H_2O + H_2.$$

Similarly, ethylene yields carbon monoxide and hydrogen:

$$C_2H_4 + O_2 = 2CO + 2H_2.$$

These results received support from the researches of Kersten [3] in 1861, and, in later years, of many other investigators. They are of particular interest in that they prove hydrogen to be no longer the "favoured" element under explosive conditions.

Kersten [4] sought to explain the phenomena on the assumption that when the hydrocarbon has been decomposed by the heat of the flame into hydrogen and carbon, the latter is preferentially oxidised to carbon monoxide, after which any excess of oxygen distributes itself between this gas and the hydrogen.

Assuming the theory of preferential combustion to be true, the question at once arises as to what factors determine whether or not a given element shall be the more "favoured." Clearly the chemical nature of the element cannot be the sole deciding factor, otherwise it is not clear why hydrogen should in certain cases be more favoured than carbon, and in other cases less so.

Although the theory of preferential combustion has not been definitely disproved, a more satisfactory

explanation of the foregoing and of other phenomena of combustion is afforded by what may be termed the **Association theory**, according to which the oxygen of the air first combines with the hydrocarbons forming more or less unstable hydroxylated products which ultimately, in a sufficiency of air or oxygen, decompose to carbon dioxide and water.

These conclusions have been arrived at by Bone and his collaborators mainly as the result of an extensive series of researches on the slow combustion of methane at temperatures ranging from 300° C. to 510° C., and receive ample support from the behaviour of mixtures of oxygen and other hydrocarbon gases under analogous conditions. The initial experiments[5] were conducted with various mixtures of gases contained in sealed bulbs of boro-silicate glass at temperatures between 300° C. and 400° C., but as the volume of gases capable of being dealt with in this manner was limited, namely about 70 c.c., and as, moreover, such a method was not adapted for the detection and isolation of transient intermediate products, later experiments[6] were conducted with the aid of a different type of apparatus. This consisted of a combustion tube filled with fragments of ignited porous porcelain through which some 1200 c.c. of the reacting gases were continuously circulated by means of a Sprengel pump which worked automatically. The experiments were protracted, in some cases extending over several weeks, during which times the following facts were definitely established:—

1. None of the reactions *a* to *f* indicated below

takes place to any appreciable extent at temperatures of 400° C. downwards.

$$
\begin{array}{ll}
(a) & C + H_2O = CO + H_2 \\
(b) & C + CO_2 = 2CO \\
(c) & 2C + O_2 = 2CO \\
(d) & 2CO + O_2 = 2CO_2 \\
(e) & CO + H_2O \rightleftharpoons CO_2 + H_2 \\
(f) & 2H_2 + O_2 = 2H_2O
\end{array}
$$

Also, the following pairs of gases were found to have no appreciable mutual action at or below 400° C., namely, $CH_4 + CO_2$, $CH_4 + H_2O$, and $CO + H_2$.

This greatly simplifies the study for, when once the methane has begun to oxidise, an indefinite number of secondary reactions might be expected to take place if the foregoing reactions were capable of proceeding with an appreciable velocity.

2. Between 300° and 400° C. methane is oxidised with comparative rapidity by oxygen gas. When insufficient oxygen is present to completely oxidise the methane, the final products are water, carbon monoxide, and carbon dioxide. Neither free hydrogen nor free carbon is produced in detectable quantities. Since, if once formed, it would be impossible for them to be oxidised away in accordance with schemes *b*, *c*, or *f*, it follows that their detection and isolation would be an easy matter, and hence it may be postulated that under normal conditions of slow combustion the methane is not first dissociated into carbon and hydrogen. It seems equally clear, moreover, that the carbon monoxide and water formed are two of the primary disintegration products

of the partial oxidation of the methane molecule at these temperatures as these are too low for reaction *f* to take place.

3. A large proportion of carbon dioxide is frequently formed, sometimes almost equal in volume to the carbon monoxide produced. Since the conditions preclude all possibility of its formation by oxidation of the monoxide either directly with oxygen or through interaction with steam (reactions *d* and *e* above), it would appear to be a disintegration product of some more complex oxygenated molecule.

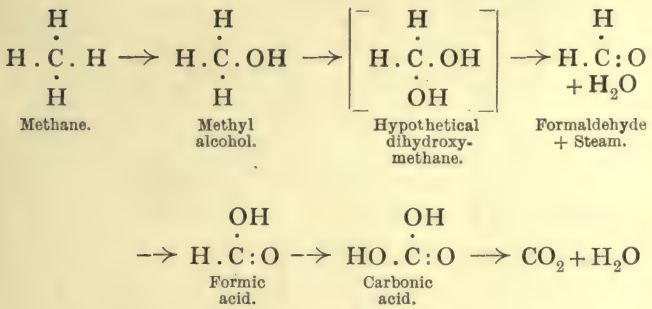
4. Formaldehyde, H.CHO, is formed during the slow oxidation of methane at 450° to 500° C. and can be detected as a transient intermediate product. Since it is not produced when mixtures of moist carbon monoxide and hydrogen are continuously circulated for two days over a hot surface of porous porcelain at 460° to 480° C.,[6, 7] it seems reasonable to suppose that it is one of the products of the slow oxidation of methane, and is not produced by minor secondary reactions. When heated, in the absence of air or oxygen, it readily decomposes into hydrogen and carbon monoxide:

$$H.CHO = H_2 + CO,$$

but there is no evidence that the reaction is reversible, although under the influence of a silent electric discharge formaldehyde may be obtained from hydrogen and carbon monoxide.[8] In the presence of air it yields carbon dioxide and water.

Piecing all this evidence together, Bone and

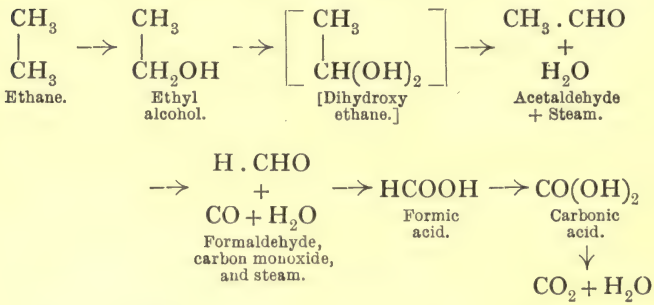
Wheeler in 1903 came to the conclusion that the slow combustion of methane takes place in several stages involving the formation and subsequent decomposition of formaldehyde, with the final production of carbon dioxide and water if sufficient oxygen is present. Armstrong,[9] however, suggested that the real initial product is not formaldehyde but methyl alcohol, which rapidly decomposes to formaldehyde and steam. This view is accepted by Bone.[10] These changes may be represented schematically as follows:—



The methyl alcohol, which, on account of its easy oxidation cannot be experimentally detected, is assumed to undergo hydroxylation to hypothetical dihydroxymethane. This instantly decomposes to formaldehyde, which, with its next hydroxylation product, namely formic acid, can easily be detected amongst the products of the slow oxidation of methane. The final stage of the oxidation is reached with the hydroxylation of formic acid to carbonic

acid, which immediately undergoes fission into carbon dioxide and water.

With ethane, C_2H_6, the mechanism of slow combustion is believed to proceed as follows[11]:—



The presence of ethyl alcohol as the primary product of oxidation of ethane has not been determined experimentally, for alcohol is, under these conditions oxidised far more rapidly than ethane itself. Ethyl alcohol has, however, been detected among the products of the interaction of ethane and ozone at 100° C., and it seems highly probable, therefore, that ethyl alcohol is really the primary product of oxidation as indicated above.[12]

Hydrogen, methane, and ethylene are sometimes[13] found amongst the products of oxidation, without, however, any carbon being liberated. Their appearance is due to the purely thermal decomposition of ethane, formaldehyde, and acetaldehyde.[14] Thus:

$$C_2H_6 = C_2H_4 + H_2$$
$$H.CHO = H_2 + CO$$
$$CH_3.CHO = CH_4 + CO$$

In the case of ethylene,[15] the reactions suggested are as follows:—

$$\underset{\text{Ethylene.}}{\overset{CH_2}{\overset{\|}{CH_2}}} \rightarrow \underset{\text{Vinyl alcohol.}}{\overset{CH_2}{\overset{\|}{CH(OH)}}} \rightarrow \underset{\text{Dihydroxy ethylene (hypothetical).}}{\overset{CHOH}{\overset{\|}{CHOH}}} \rightarrow \underset{\text{Formaldehyde.}}{2H.CHO}$$

$$\rightarrow \underset{\text{Formic acid.}}{H.COOH} \rightarrow \underset{\text{Carbonic acid.}}{CO(OH)_2} \rightarrow CO_2 + H_2O$$

Vinyl alcohol could not, of course, be experimentally detected among the products.

Acetylene appears to react as follows [16]:—

$$\underset{\text{Acetylene.}}{\overset{CH}{\overset{\|\|}{CH}}} \rightarrow \overset{C(OH)}{\overset{\|\|}{CH}} \rightarrow \overset{C(OH)}{\overset{\|\|}{C(OH)}} \rightarrow \underset{\text{Formaldehyde + Carbon monoxide.}}{\overset{H.CHO}{\overset{+}{CO}}}$$

$$\rightarrow \underset{\text{Formic acid.}}{H.COOH} \rightarrow \underset{\text{Carbonic acid.}}{CO(OH)_2} \rightarrow CO_2 + H_2O$$

It seems reasonable to conclude that during rapid combustion of the hydrocarbon gases, closely similar reactions obtain.

Combustion of Carbon Monoxide.

Lavoisier demonstrated the general principle that the increase in weight of the products of combustion

in air is equal to the weight of oxygen consumed. From this date until 1880, chemists regarded the combustion of carbon monoxide as a simple straightforward chemical change, represented by the equation

$$2CO + O_2 = 2CO_2.$$

In his address to the Chemical Section of the British Association in 1880, however, Dixon[17] pointed out that dry carbon monoxide and dry oxygen do not unite. A trace of water must be present. Neither dry carbon dioxide, nitrogen, nor cyanogen was found to have any effect, but such gases as hydrogen, hydrogen sulphide, ether vapour, ethylene, ammonia, etc., act in a similar manner to water vapour. In other words, all substances that will form steam under the conditions of the experiment are capable of determining the combustion.

Dixon, therefore, suggested that "in the ordinary combustion of carbonic oxide," the steam present acts the part of a "carrier of oxygen" by undergoing reductions and successive re-formations:—

$$(1)\ CO + H_2O = CO_2 + H_2$$
$$(2)\ 2H_2 + O_2 = 2H_2O.$$

Traube[18] disputed the generalisation. He pointed out that the reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

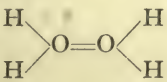
is reversible, and at the temperature of the electric spark proceeds from right to left. He therefore

argued that Dixon's hypothesis must be incorrect.[19] Having observed that hydrogen peroxide is obtained when moist carbon monoxide is burned, Traube concluded that the reactions were as follows:—

$$CO + OH_2 + O_2 = CO_2 + H_2O_2$$
$$CO + H_2O_2 = CO_2 + H_2O.$$

It has also been suggested[20] that percarbonic acid, $H_2C_2O_6$, is formed as an intermediate product, and this is supported by the fact that a flame of carbon monoxide impinging on water containing a little potassium hydroxide and cobalt chloride gives a precipitate identical with that obtained with the same mixture on addition of potassium percarbonate. But this test alone is not conclusive since potassium hydrogen carbonate gives the same precipitate with hydrogen peroxide in the presence of cobalt chloride.[21]

Bone,[24] in discussing the influence of hydrogen upon the rate of explosion of mixtures of carbon monoxide and oxygen, suggests that carbon monoxide is incapable of combining directly with *molecular* oxygen. The hydrogen serves to induce the formation of either nascent oxygen or "activated" steam molecules, both of which can oxidise the monoxide. It is assumed that oxygen molecules unite in the flame each with four atoms of hydrogen to yield the unstable dihydrol complex



which instantly dissociates into a mixture of free hydrogen molecules, nascent oxygen, and nascent or

"activated" steam. The carbon monoxide is then oxidised as follows:

$$CO + :O = CO_2$$
$$CO + :OH_2 = CO_2 + H_2$$

Bone does not apply this to a direct consideration of the influence of steam upon the oxidation of carbon monoxide, but since steam dissociates at the temperature of flames into hydrogen and oxygen it is easy to see how the above reactions could take place and the oxidation of carbon monoxide be thereby facilitated.

The Combustion of Cyanogen.

Cyanogen burns in a Smithells' separator with characteristic beauty.[22] The inner flame is red, the cyanogen burning to carbon monoxide. Thus:

$$C_2N_2 + O_2 = 2CO + N_2.$$

The outer flame is blue, the carbon monoxide now undergoing further oxidation to the dioxide.

The Combustion of Hydrogen.

It is a remarkable fact that although hydrogen and oxygen unite with explosive violence when a spark is passed into the mixed gases, yet the pure gases dried over phosphorus pentoxide do not explode, even on heating to redness.[23] Even at the melting-point of silver (960° C.) no combination takes place. This is a typical example of the curious fact that, as the methods of preparing pure substances become increasingly refined, the number of reactions known to occur between the impure reagents, but not between them or only with excessive slowness when in a state of high purity, is steadily increasing.

SECTION VI.

Ignition Temperatures.

The **ignition temperature** has already been defined (see p. 6) as that temperature at which rapid combustion becomes independent of external supplies of heat.

The temperature of ignition is the temperature at which the heat evolved by the reaction just equals and therefore counterbalances the loss of heat consequent upon radiation, etc.

A clear idea[1] may be obtained by imagining a combustible mixture of gases to issue from an orifice into an inert atmosphere.[2] If the orifice is surrounded by a ring of platinum wire which is being raised in temperature by passage of an electric current, a flame will gradually make its appearance. If, as soon as this is observed, the heating of the wire by the electric current be discontinued, the flame will disappear. It is not self-supporting, but depends upon the accessory supply of heat from the electrically heated wire. If now we raise the ring to a still higher temperature than before, a brighter flame is obtained in consequence of the increased rate of chemical action; and finally a temperature is reached at which the flame will continue to burn without the aid of any heat from the wire, so that the current may be cut off. This is the temperature of ignition.

Attention has already been directed to the phenomena of spontaneous combustion. When, for example, liquid phosphoretted hydrogen, P_2H_4, or zinc ethyl, $Zn(C_2H_5)_2$, is allowed to come into contact with air, it spontaneously bursts into flame. The ignition temperatures of these bodies lies below the usual temperature of the atmosphere. The ignition temperature of pure gaseous phosphoretted hydrogen, PH_3, lies below 100° C., and a sample of the gas prepared by the action of alcoholic potash upon phosphorus if allowed to escape from a jet, may be ignited by causing it to impinge upon a test-tube of boiling water. The vapour of carbon disulphide ignites at a slightly higher temperature, namely, at about 120° C. If, therefore, a hot glass rod is introduced into a beaker containing a few drops of carbon disulphide, the vapour immediately inflames.

Hydrogen ignites in air more readily than coal-gas, and this is readily shown by allowing the latter to impinge upon a warmed bundle of platinised asbestos, when the latter becomes red hot, but does not usually effect the ignition of the gas.[13] If, however, the coal-gas be replaced by hydrogen, the latter immediately inflames.

The earliest systematic attempts to determine the ignition temperatures of various gases were those of Davy,[3] who observed that hydrogen could be inflamed at the "lowest visible heat of iron," that is approximately 500° C. Ethylene and carbon monoxide inflamed at red heat (probably *c.* 700° C.), whilst methane required contact with an iron rod in brilliant combustion. Modern methods of deter-

mining ignition temperatures may be divided into five main groups, namely :—

I. The combustible mixture of gases is contained in glass bulbs and raised in temperature by immersing in a heated bath.[4]

Under these conditions the gases are fired under pressures usually somewhat greater than atmospheric, and in contact with a relatively large superficial area of glass which may act catalytically upon the reaction. This method has also been adopted for slow combustion experiments, but, in consequence of the catalytic action just referred to, different investigators have frequently obtained widely different results. Thus, for example, with electrolytic gas, Meyer and Raum[4] made the following observations :—

Temperature.	
100° C . .	No water detectable after 218 days.
300° . .	Water detected in 65 days.
350° . .	Water detected in 5 days.
448° . .	Perceptible action, but very slow.

On the other hand, Bone and Wheeler[4] have succeeded in keeping electrolytic gas in glass bulbs at 400° C. for seven days without observing any combination of the gases, although in some of their experiments the presence of water could be detected. It would thus appear that 400° C. is the border-line for the slow combustion of hydrogen and oxygen under these conditions within finite time.

II. A second method consists in passing a stream of the combustible mixture of gases through a tube which is gradually heated up until the gases ignite.[5] This method has the advantage of yielding results at the normal pressure of the atmosphere, but is still

liable to be influenced by the catalytic action of the walls of the tube. Further, the gases are not at rest, but in motion.

III. A particularly valuable method is that devised by Dixon[6] in 1903 and shown diagrammatically in Fig. 9.

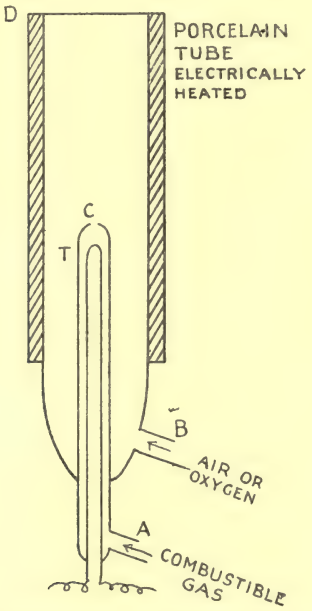


FIG. 9.—Dixon's Apparatus for determining Ignition Temperatures of Gases.

The principle of this method consists in heating the combustible gases separately to such a temperature that they immediately inflame upon coming into contact. The combustible gas was admitted to the apparatus at A and the atmosphere of air or

oxygen at B. During passage up the tubes the gases attained the temperature registered by the thermocouple in T and began to mix at C, from which orifice the combustible gas issued. The porcelain tube, D, 4·5 cms. in diameter, surrounded by platinum wire and asbestos packing, was electrically heated, the temperature being allowed to rise at the rate of 5° C. per minute, until the issuing gas at C. inflamed in contact with the air.

This method, like the previous one, gives results at atmospheric pressure, but possesses the further advantages that the *mixed* gases are only momentarily in contact with a possible catalyst, namely, the small orifice at C.

Experiment showed that, on working with different furnace tubes, a constant ignition-point was obtained when both the diameter of the outer tube and the rate of passage of the combustible gas through the orifice were made to exceed a certain minimum value.

The following results were obtained:—

Gas.	Ignition Temperature, °C.	
	Oxygen.	Air.
Hydrogen	580 to 590	580 to 590
Carbon monoxide (moist)	637 ,, 658	644 ,, 658
Methane	556 ,, 700	650 ,, 750
Ethane	520 ,, 630	520 ,, 630
Propane	490 ,, 570	...
Ethylene	500 ,, 519	542 ,, 547
Acetylene	416 ,, 440	406 ,, 440
Cyanogen	803 ,, 818	850 ,, 862
Hydrogen sulphide	220 ,, 235	346 ,, 379
Ammonia	700 ,, 860	...

It will be observed that in the majority of cases the ignition temperature in air is practically identical with that in oxygen.

IV. Adiabatic compression.[7] As is well known, when gases are compressed, heat is evolved, and if the rate of compression is sufficiently rapid to prevent the undue escape of heat, the gases will rise in temperature. By suitably arranging the apparatus the gases may be fired, and if the volume of the gases at the moment of firing can be determined, their temperature—the ignition temperature under compression—admits of calculation from the well-known equation

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1},$$

T representing the absolute temperature, V the volume, and γ the mean ratio of the specific heats of the gaseous mixture at constant pressure and volume. The essential features of the apparatus used by Dixon and Crofts[7] are shown in outline in Fig. 10.

The body of the apparatus consisted of a steel cylinder 56 cms. in length and 11 cms. in diameter, with a cylindrical cavity 3·02 cms. in diameter through its axis. The lower end of this cavity was opened out and threaded to enable a plate to be inserted to close the bottom of the cylinder and to be kept in place by a powerful screw. The combustible mixture of gases was introduced into the apparatus through a tube A, and the upper end of the cylinder was closed with a plug attached to a piston, bearing a head, H, of great strength, upon

which an iron block, weighing 76 kg. (2½ cwts.), was allowed to fall from a height of about 1·5 metres.

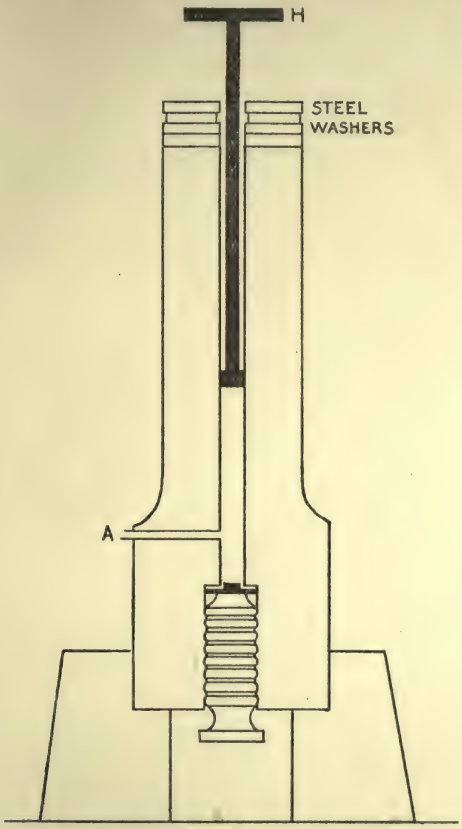


Fig. 10.—Dixon and Crofts' Apparatus for determining Ignition Temperatures by Compression.

This sufficed to drive the plug well down the cylinder and so to compress the gases. The extent

of compression was regulated by a series of steel washers which could be arranged to catch the piston head at any desired position during its descent.[8] The initial and final volumes being thus known, the temperature after compression was calculated by means of the equation given above, γ being taken as 1·4. The temperature of ignition was found by "trial and error," the compression being increased or decreased in successive trials until ignition just took place.

The following results were obtained :—

Relative Volumes of the Gases.	Ignition Temperature, °C.
$2H_2+O_2$	526
$2H_2+2O_2$	511
$2H_2+8O_2$	478
$2H_2+16O_2$	472
$2H_2+32O_2$	never exploded

These results are not, of course, strictly comparable with those obtained by the previous method, owing to the high pressures developed, these being of the order of 30 atmospheres. The temperatures obtained are appreciably lower than that found for the ignition of hydrogen in oxygen by Method III.

V. The Soap Bubble Method. This exceedingly ingenious device adopted by M'David[9] in 1917 consists in blowing soap bubbles with the combustible gaseous mixture and allowing them to impinge upon an electrically heated wire, the temperature of which is raised until the gases ignite. The

results obtained by this method are high and are regarded as not very reliable.[10]

In the following table are given the results obtained by M'David, and these where possible are compared with those obtained by Dixon and Coward by Method III.

Gaseous Mixture.	M'David.	Dixon and Coward.
	°C.	°C.
Hydrogen-air . . .	747	580 to 590
Carbon monoxide-air .	931	637 ,, 658
Ethylene-air . . .	1000	500 ,, 519
Coal-gas-air . . .	878	...
Benzene-air . . .	1062	...
Ether-air	1033	...
Petrol-air	995	...

It will be seen that not only does a wide difference exist between the different sets of results, but the temperatures do not follow the same relative order. Thus, M'David finds the ethylene to have a higher ignition temperature than either hydrogen or carbon monoxide, whilst Dixon and Coward found it to be lower.

In the table on pp. 56 and 57 are given the more important results obtained by the various methods described for the ignition temperatures of gases.

The temperature at which the vapour of a liquid forms an inflammable mixture with air is frequently termed its **flash-point**, and its accurate determination is often a matter of considerable legal importance, more particularly in the case of low flash-point paraffin oils sold for domestic illuminating purposes.

Gases.	Ignition Temperature, °C.	Method.	Authority and Date.
Hydrogen-oxygen .	518 to 606	I	Krause and Meyer (1891).
	589	I	Emich (1900).
	650 to 730	II	Meyer and Freyer (1892).
	620 ,, 680	II	Meyer and Münch (1893).
	550	II	Mallard and Le Chatelier (1880).
	653 to 710	II	Bodenstein (1899).
	674	II	Mitscherlich (1893).
	840	II	Gautier and Hélier (1896).
	845	II	Hélier (1897).
	580 to 590	III	Dixon and Coward (1909).
$2H_2+O_2$ . . .	540	IV	Falk (1906).
$2H_2+2O_2$ . .	514	IV	,, ,,
$2H_2+4O_2$ . .	530	IV	,, ,,
$2H_2+O_2$ . . .	526	IV	Dixon and Crofts (1914).
$2H_2+2O_2$ . .	511	IV	,, ,,
$2H_2+8O_2$ . .	478	IV	,, ,,
Hydrogen-air . .	580 to 590	III	Dixon and Coward (1909).
	747	V	M'David (1917).
Methane-oxygen .	606 to 650	I	Meyer and Freyer (1893).
	650 ,, 730	II	,, ,,
	656 ,, 678	II	Meyer and Münch (1893).
	556 ,, 700	III	Dixon and Coward (1909).
Methane-air . .	650 ,, 750	III	,, ,,
Ethane-oxygen .	530 ,, 606	I	Meyer and Freyer (1893).
	606 ,, 650	II	,, ,,
	605 ,, 622	...	Meyer and Münch (1893).
	520 ,, 630	III	Dixon and Coward (1909).
Ethane-air . .	520 ,, 630	III	,, ,,
Propane-oxygen .	545 ,, 548	II	Meyer and Münch (1893).
	490 ,, 570	III	Dixon and Coward (1909).
Ethylene-oxygen .	530 ,, 606	I	Meyer and Freyer (1893).
	606 ,, 650	II	,, ,,
	577 ,, 590	II	Meyer and Münch (1893).
	500 ,, 519	III	Dixon and Coward (1909).

Gases.	Ignition Temperature, °C.	Method.	Authority and Date.
Ethylene-air . .	542 to 547	III	Dixon and Coward (1909).
	1000	V	M'David (1917).
Acetylene-oxygen .	509 to 515	II	Meyer and Münch (1893).
	416 ,, 440	III	Dixon and Coward (1909).
Acetylene-air . .	406 ,, 440	III	,, ,,
Propylene-oxygen .	497 ,, 511	II	Meyer and Münch (1893).
Isobutane-oxygen .	545 ,, 550	II	,, ,,
Isobutylene-oxygen	537 ,, 548	II	,, ,,
Coal-gas-oxygen .	647 ,, 649	II	,, ,,
Coal-gas-air . .	878	V	M'David (1917).
Benzene-air . .	1062	V	,, ,,
Ether-air . .	1033	V	,, ,,
Cyanogen-oxygen .	803 to 818	III	Dixon and Coward (1909).
Cyanogen-air . .	850 ,, 862	III	,, ,,
Carbon monoxide-oxygen	650 ,, 730	I	Meyer and Freyer (1893).
	650 ,, 730	II	,, ,,
	637 ,, 658	III	Dixon and Coward (1909).
Carbon monoxide-air	644 ,, 658	III	,, ,,
	931	V	M'David (1917).
Hydrogen sulphide-oxygen	250 to 270	I	Meyer and Freyer (1893).
	315 ,, 320	II	,, ,,
	220 ,, 235	III	Dixon and Coward (1909).
Hydrogen sulphide-air	346 ,, 379	III	,, ,,
Ammonia-oxygen .	700 ,, 860	III	,, ,,
Hydrogen-chlorine .	240 ,, 270	I	Meyer and Freyer (1893).
	430 ,, 440	II	,, ,,

An elaborate and carefully standardised apparatus is then necessary.

A determination of the flash-point of an oil is frequently desirable as a check upon its purity. Thus, for example, linseed oil has normally a flash-point of 250° C., but if adulterated with rosin oil, of usual flash-point 155° to 160° C., the presence of this latter oil is readily detected in this way. This is a great advantage, because although rosin oil is denser than linseed, the density of the mixture could easily be "doctored" by addition of some other lighter ingredient which would render gravity determinations useless.

A convenient rough method of determining the flash-point consists in heating the oil in the inner pot of a glue pot, the outer one serving as an air-bath. A thermometer is inserted in the oil and a small gas jet made from a mouth blow-pipe is brought close to but not actually touching the surface of the oil. The temperature is taken at which a small blue flame is seen to flash for the first time across the oil. This is the flash-point. In the following table are given the approximate flash-points of several well-known liquids:—

Liquid.	Flash-point, °C.
Linseed oil	250
Rosin oil	155 to 160
Paraffin illuminating oils	38 ,, 50
Turpentine	35 ,, 40
Rosin spirit	35 ,, 40
Naphtha	16 ,, 21
Methylated spirit	14 ,, 16

The ignition temperatures of a few substances that are solid at the ordinary temperature have been determined, and a few of the more interesting data are given in the accompanying table, together with the melting- and boiling-points of the substances concerned [11]:—

Substance.	Melting-point, °C.	Ignition Temperature, °C.
Carbon—Diamond . .	*c.* 3500	800 to 850
Graphite . .	,,	690
Amorphous . .	,,	345
Phosphorus, Yellow . .	44·5	*c.* 60
,, Red . . .	...	255 to 260
Sulphur in air [12] . . .	119·2	255
,, in oxygen [12] . .	...	257 to 264

SECTION VII.

The Inflammation of Gaseous Mixtures.

Upon introducing a source of heat into a combustible mixture of gases, two conditions must be satisfied in order to ensure propagation of the flame throughout the mixture.

(*a*) The initial source of heat must be of sufficient volume, intensity, and duration to raise the adjacent layer of combustible gases to at least their ignition temperature.

(*b*) The heat resulting from the combustion of this layer must be sufficient in turn to raise the next adjacent layer to its temperature of ignition, and so on.

Any excess of one of the constituent gases over that required for complete combustion will serve as a diluent, and if the excess is very great the heat absorbed in raising the temperature of the mixture may be so large as to prevent the attainment of the ignition temperature. The largest quantity of the diluent which may be present and yet allow a flame to be propagated from layer to layer throughout the mixture without the continued presence of the original source of heat, is a measure of the **limit of inflammation.** The majority of the researches on

this branch of our subject have been carried out with gases that are combustible in air or oxygen, and it is to these that our attention will now be directed.

An interesting example is afforded by ammonia vapour which readily burns in oxygen but not in ordinary air. If a taper is applied to ammonia vapour as it issues from a jet, the characteristic livid

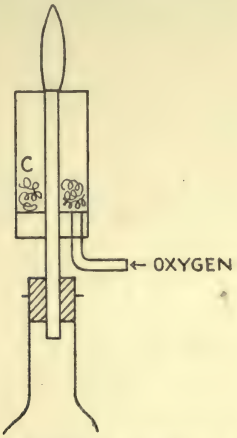


FIG. 11.—Combustion of Ammonia Vapour in Air enriched with Oxygen.

flame of the gas is seen burning side by side with the flame of the taper. But combustion at once ceases when the taper is withdrawn. If, however, the jet is surrounded by oxygen or air enriched with this gas, the ammonia may be made to burn continuously even after the removal of the taper. This is conveniently shown by means of the apparatus figured above.

Concentrated ammonia solution is gently warmed in the flask and the escaping vapour is surrounded by air enriched with oxygen which enters the circumscribing cylinder and is distributed round the central tube by the glass wool C. If, before passage of oxygen, a lighted taper is applied, the ammonia vapour is seen to burn alongside of the flame of the taper, but immediately the taper is removed combustion ceases. On adding increasing quantities of oxygen, the ammonia flame grows stronger until eventually the taper may be removed and the ammonia continues to burn without requiring any external source of heat. The minimum quantity of oxygen required to maintain this condition is termed the **lower oxygen limit of inflammation.**

By the **lower limit of inflammation** is understood the smallest quantity of any combustible gas which, when mixed with air or oxygen, will admit of this self-propagation of flame. But there is also a **higher limit of inflammation**, for clearly if the combustible gas is in excess, the excess will function as a diluent, and the higher limit thus becomes the lower oxygen or atmosphere limit.

Some of the earliest work on the subject was that of Davy[1] in 1816, whose experiments indicated a lower limit of inflammation of fire-damp in air as one part in 16 or 17, that is between 6·3 and 6·7 per cent. Modern researches have been carried out in three different ways, namely:—

1. The gases are ignited by passing an electric spark between terminals placed at the centre of a large glass globe containing the combustible

mixture. This was the method adopted by Burgess and Wheeler[2] in 1911, their apparatus being shown in Fig. 12.

The globe had a capacity of approximately 2 litres and was fitted with platinum electrodes which entered the globe through ground stoppers. The method of experiment consisted of "trial and error," the proportion of combustible gas being successively reduced or increased until two mixtures were obtained,

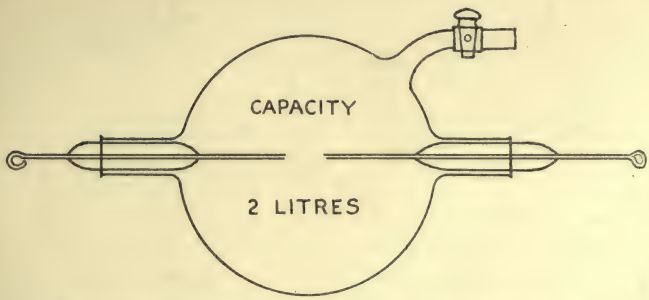


FIG. 12.—Apparatus used by Burgess and Wheeler (1911).

one of which just enabled the flame to be propagated whilst the other did not. The authors[3] found that the lower limit mixture could be distinguished with certainty from that containing a slightly insufficient proportion of combustible gas, because the first sparking produced in the former case inflammation of all the gas in the globe, and on further sparking no further sign of combustion was manifest. In the latter case, on the other hand, although the flame might appear to travel pretty well through the globe with the first spark, a "cap" would appear upon

sparking a second time, showing that the whole of the combustible gas had not disappeared.

2. The gases may be electrically ignited in a horizontal tube closed at both ends. For this purpose a tube about 6 cms. in diameter is convenient, the flame steadily creeping along the upper walls in some such manner as that indicated in Fig. 13, as the lower limit is approached.[4]

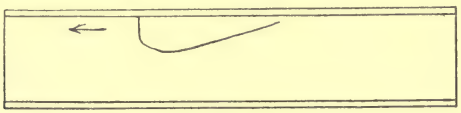


Fig. 13.

3. A vertical tube may be employed, closed at both ends and ignited electrically either at the top or at the bottom.

Method.	Lower Limit. Methane per cent.	Higher Limit. Methane per cent.
1. Globe	5·6	14·8
2. Horizontal tube . .	5·4 flame travels only along top of tube. 5·6 methane all combusted.	14·3
3. Vertical tube :—		
(*a*) Top ignition .	6·0	13·4
(*b*) Bottom ignition .	not < 5·4	not > 14·8

As is to be anticipated, these methods do not all give quite the same result. Owing to convection currents, a low value for the lower limit and a high value for the higher limit are obtained by bottom gnition in a vertical tube, whilst top ignition yields

a high value for the lower limit and a low value for the higher limit. These differences are well illustrated by the results obtained by Burgess and Wheeler[4] for mixtures of methane and air.

The lower limit mixture depends upon a variety of factors, the more important of which are as follows:—

(*a*) The calorific power of the gas, which may be designated as C.

(*b*) The relative volume and specific heat of the diluent.

(*c*) The ignition temperature of the combustible gas.

(*d*) The pressure. Increase of pressure raises the higher and lower limits,[5] as is evident from the following data for methane in air:—

Pressure, cm. Mercury.	Lower Limit. Methane per cent.	Higher Limit. Methane per cent.
76	6·0	13·0
125	6·05	13·15
290	6·2	13·6
465	6·4	14·05

(*e*) The temperature. Rise of temperature tends to reduce the lower limit value, as theoretical considerations would lead us to expect. This is evident from the data given below, which refer to methane in air.[6]

Temperature, °C. .	20	175	237	312	555	690
Lower Limit. Methane per cent.	5·80	5·25	4·75	4·30	3·40	3·00

(*f*) In the case of the inflammation of gaseous mixtures in horizontal or vertical tubes, the diameter of the tubes exerts an important influence if less than about 5 cms. This is well illustrated by the data obtained for acetone[7] in air.

Diameter of Tube.	Lower Limit. Per cent. Acetone.			Higher Limit. Per cent. Acetone.		
	Horizontal.	Downward.	Upward.	Horizontal.	Downward.	Upward.
cm.						
2·5	2·40	2·75	2·30	6·7	6·5	7·5
5·0	2·25	2·40	2·20	9·3	8·3	9·5
10·0	2·20	2·35	2·15	9·5	8·5	9·7

It is of interest to inquire whether or not the lower limit concentration of a combustible gas in air can be calculated, making due allowance for the above factors.[8] Assuming *d* and *e* to represent the average pressure and temperature of the atmosphere, and either *f*, the diameter of the tubes, to remain constant, or the values for the lower limits in the globe experiments, only, to be considered, it is evident that factor *a*, the calorific power of the combustible gas is the most important of the remaining factors in the majority of cases. Writing L as the proportion of combustible gas in a lower limit mixture, it is to be anticipated that L should be some function of 1/C. If strict proportionality obtains, which is very possible for analogous gases such as those of the saturated hydrocarbon series, then $L \propto 1/C$ or $L = K/C$. Taking methane as the

standard, for which L = 5·6 and C = 189·1, we arrive at the value

$$K = LC = 1059.$$

Using this value for K, L may be calculated for the other saturated hydrocarbon gases from their calorific values determined by Thomsen. This is done in the following table[8]:—

Gas.	Calorific Value.	L determined by the Globe Method.	L calculated.
Methane . .	189·1	5·60	standard
Ethane . . .	336·6	3·10	3·15
Propane . .	484·2	2·17	2·19
n-Butane . .	631·7	1·65	1·68
n-Pentane . .	779·2	1·37	1·36
Isopentane . .	779·2	1·32	1·36

The agreement is surprisingly close; but when this method of calculation is applied to other combustible gases, such as hydrogen[9] (L = 10·0), using the above value for K, serious discrepancies arise. But this is to be anticipated, for there is no reason why L should be directly proportional to C—an assumption upon which the calculated value for K rests.

A few experiments have been carried out with a view to determining the composition of the atmosphere that extinguishes flames. It appears that the extinction of a flame is not determined only by the proportion of the "inert" gas and oxygen in the surrounding atmosphere. The nature of the inert gas also plays an important part in determining the lower oxygen limit. Thus, for example, carbon dioxide is found to exert a more powerful extinctive effect than nitrogen.

The composition of the extinctive atmosphere produced by a candle flame is as follows[10]:—

	Per cent.
Oxygen	15 to 16
Nitrogen	80 ,, 81
Carbon dioxide . . .	3

This closely corresponds to the average composition of the air expired by human beings, and may be breathed by most people without producing any distinctly noticeable ill-effect.

Other results of interest are[11]:—

Combustible Substance.	Residual Air contains.
	Per cent.
Candle burned until extinguished	4 to 6 CO_2 13 ,, 15 oxygen
Alcohol burning on cotton-wool to extinction	6·5 CO_2 11 oxygen
Wood-charcoal glowing to extinction	8 CO_2 9 oxygen
Sulphur burning to extinction .	13·5 oxygen

Decrease of pressure raises the lower oxygen limit, as is evident from the following data[12]:—

Combustible Substance.	Extinction percentage of Oxygen.	Total Pressure of Gases.
		mm.
Ethyl alcohol burning from asbestos wick	15·1 19·0	736·7 129
Candle	16·1 19·9	736·7 91

SECTION VIII.

Propagation of Flame in Gaseous Mixtures.

A thorough knowledge of the rate of propagation of flame in mixtures of air and various inflammable gases, especially hydrocarbons, is eminently desirable in view of the ever-present danger of serious fires and explosions in coal-mines.

When an explosive mixture of gases contained in a horizontal tube closed at one end is ignited at the open end, it is observed [1] that:—

1. A flame travels a certain distance along the tube with a uniform and relatively slow velocity. In the case of acetylene and air this distance is small; with methane and air it is relatively long.
2. Vibrations are gradually initiated which become increasingly intense, the flame moving backwards and forwards with oscillations of ever-increasing amplitude.
3. The flame either dies out or the remainder of the gas in the tube detonates, initiating what is termed the *explosion wave*.

It is thus evident that a flame may be propagated throughout a gaseous mixture in two ways, namely :—

A. With a relatively slow motion, characterised by its uniformity, and

B. With a rapid explosion wave, usually accompanied by detonation.

It is proposed to deal briefly with each of these in this section.

A.—Uniform Slow Movement in the Propagation of Flame in Gaseous Mixtures.

The conditions most favourable for obtaining and preserving the initial uniform movement of flames are given [2] as follows :—

1. The inflammable mixture should be contained in a long, straight, horizontal tube open at one end and closed at the other.
2. Ignition should be effected at the open end of the tube by a source of heat not greatly exceeding in temperature the ignition temperature of the mixture, and not productive of mechanical disturbance of the mixture.

The speed of the uniform movement then depends upon four factors, to wit :—

(*a*) The diameter of the tube.

(*b*) The material of which the tube is made. (This is negligible for tubes above a certain small diameter.)

(*c*) The source of ignition.

(*d*) The composition of the gaseous mixture.

Given constancy of the first three factors, the flame speed of a given mixture may be regarded as a definite physical constant for that mixture.

Method of Experiment.

The method adopted by Wheeler[3] and his co-workers for recording the speed of the flames and the general mode of procedure may be briefly summarised as follows:—

Tubes of different materials, but frequently of glass, measuring several metres in length, of diameter ranging from 2 mm.[4] to 96·5 cms.[5] (internal measurement) and open at both ends, are fixed horizontally in a straight line. The ends are flanged and ground to receive flanged end-pieces which are held in position by metal clips. Each end-piece is fitted with a wide-bore three-way tap. Glass-covered platinum electrodes reaching to the centre of the tube, leaving a spark gap of $\frac{3}{8}$ mm. are fused 4 cms. from one end (E in the figure). Screen wires of metallic copper,[6] 0·025 mm. in diameter, are threaded vertically across the tube through fine

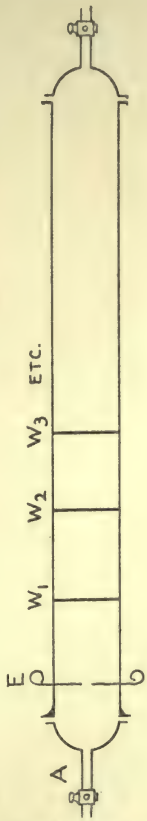


FIG. 14.—Apparatus used by Wheeler and his co-workers.

holes bored into the walls and afterwards sealed with adhesive material. In order to avoid any irregularity in the speed of the flame consequent upon the impetus that might be given by the igniting spark, the first screen wire, W_1, is fixed some 40 cms. from E, and other screen wires, W_2, etc., are fixed 50, 100, 200, 300, and 400 cms. respectively from the first. It is convenient to employ an electrical method of recording the time of passage of flame along the tube. An electric current is passed through the screen wires raising them to nearly red heat, so that they rapidly melt as soon as the flames touches them. The current is thus instantly interrupted and the time automatically recorded by the chronometer. This method appears to yield very uniform results.

In beginning an experiment, the two end taps are opened and a rapid current of the desired mixture of gases passed through. The taps are now closed, and the left hand end-piece, A, is removed by sliding it downwards very gently in such a manner as not to disturb the quiescent gaseous mixture in the tube. A spark is passed through E, whereby the mixture is ignited at the now open end of the tube.

In experimenting with gases yielding flames of sufficient actinic power to affect a photographic plate, photographic methods may be employed, a revolving drum bearing the film.

In the case of the combustion of carbon disulphide with oxygen or nitric oxide the flames are highly actinic, and in consequence readily photographed.[7] It is possible also to obtain photographs in the case of acetylene and air, and in this latter case it is a

particular advantage, as the uniform speed soon gives place to the explosion wave, and may only cover a matter of 20 cms. in the tube, so that the percentage error in the screen fusion method is abnormally great. By photography a permanent record is obtained, which can be examined at leisure,

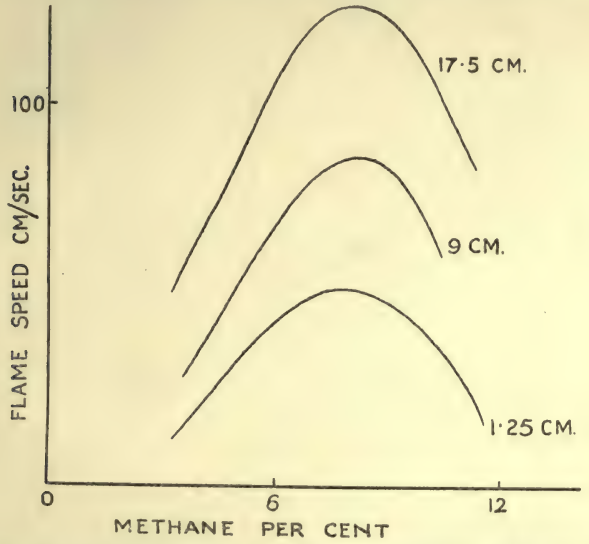


FIG. 15.—Velocity of Flame in various percentages of Methane—Air Mixtures in Tubes of different Diameters (Parker).

the rate of motion being readily determined by markings made on the photographic film with a tuning-fork.

The size of the tube exerts an important influence upon the rate of propagation of the flame.[8] In the case of mixtures of methane and air, for example,

if the diameter of the tube is small, say, of the order of 2·5 cms., the velocity of the flame is greatly retarded by the cooling effect of the walls. Where, on the other hand, the diameter is increased above 10 cms. convection currents tend to unduly accelerate the velocity of the flame, which now exhibits a

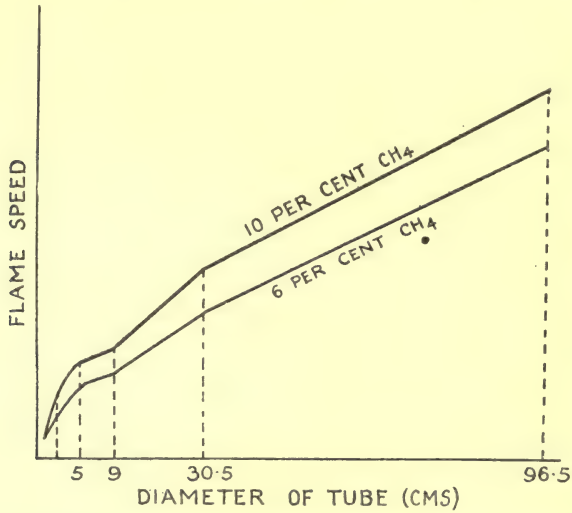


Fig. 16.—Influence of Diameter of Tube upon Flame Speed (Mason and Wheeler).

turbulent front. The flame appears to possess a swirling motion in a direction nearly perpendicular to the direction of translation of the flame front. This is caused by the rapid movement of the hot gases from below upwards by convection. In tubes of from 5 to 9 cms. in diameter this rapid movement is suppressed, although the shape of the flame front

indicates the existence of a definite movement of the hottest gases towards the upper part of the tube.

Some of the results obtained by Parker and by Mason and Wheeler are given in Figs. 15 and 16, in the latter case the diameter of the tube being plotted against the flame speed.

It will be observed that in the neighbourhood of

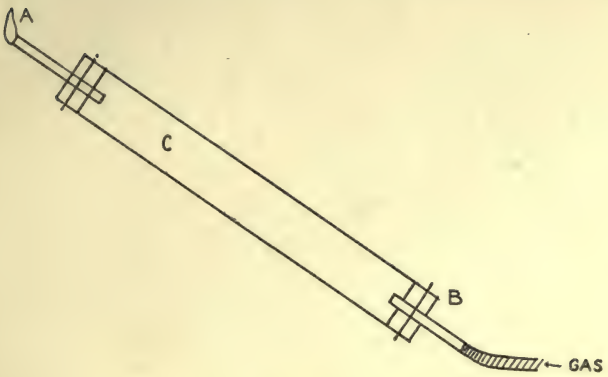


Fig. 17.

9 cms. there is a slowing up in the influence of diameter upon flame speed.

But this is only temporary, for further increase in the diameter shows that the maximum has not been reached even at 96·5 cms.

There is, on the other hand, a lower limit to the size of the tube that will allow a flame to traverse it. If the tube is diminished in size, a point is reached at which the flame will traverse only a few centimetres, and with further reduction the flame

will not pass along at all. The material of the tube in these cases plays an important part, metallic tubes being better conductors of heat, cool the flame, and prevent the passage of the flame more readily than glass. This may be conveniently demonstrated by connecting a slanting tube, as shown in Fig. 17, with the gas supply, and igniting the gas as it issues from the narrow tube at A.

The cork at B is then removed and the gas simultaneously cut off. The flame, if tube A is not too small, will pass down and a slight explosion take place in C. By employing different tubes at A the influence of size and material can easily be demonstrated.

This, of course, is the principle of the Davy Safety Lamp, to which reference has already been made, for wire gauze may be regarded as a series of thin slices of narrow tubes joined together transversely.

Variation of Gaseous Mixture.

When ignited under precisely similar experimental conditions, the velocity of the uniform movement of the flame rises as the percentage of combustible gas increases above its lower limit value, a maximum velocity being ultimately attained, after which further increase of the combustible gas effects a reduction in velocity until the higher limit concentration value is reached, when the flame ceases to pass.

This is well illustrated by the curves in Fig. 18, which depict the results of several series of experi-

ments carried out with varying mixtures of methane, oxygen, and a neutral gas—nitrogen—to serve as diluent.[9]

It will be observed that by increasing the proportion of oxygen not only does the concentration of methane at the lower limit fall slightly, but there is a very

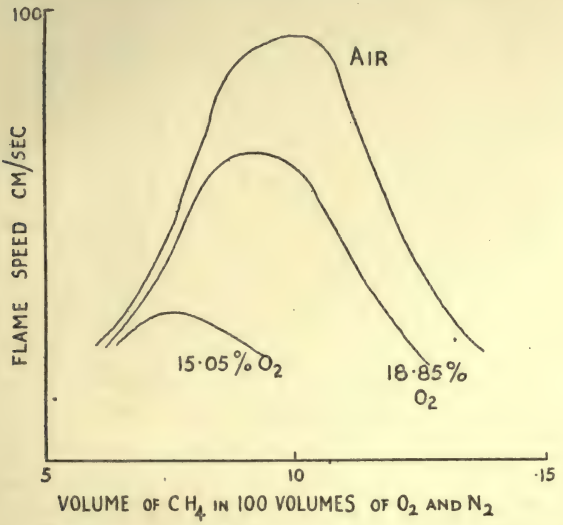


FIG. 18.—Flame Speeds of Mixtures of Methane in Oxygen and Nitrogen (Mason and Wheeler).

great increase in the upper limit concentration, provided the proportion of oxygen in the oxygen-nitrogen mixture is less than about 25 per cent. With oxygen-nitrogen mixtures containing more than 25 per cent. oxygen, the lower limit of methane rises slightly.[10a]

Further, the methane concentration yielding the maximum flame speed rises with the proportion of oxygen, and yields a greatly enhanced flame speed. Similar results are obtained with mixtures of methane and air, the latter being enriched with oxygen.[10]

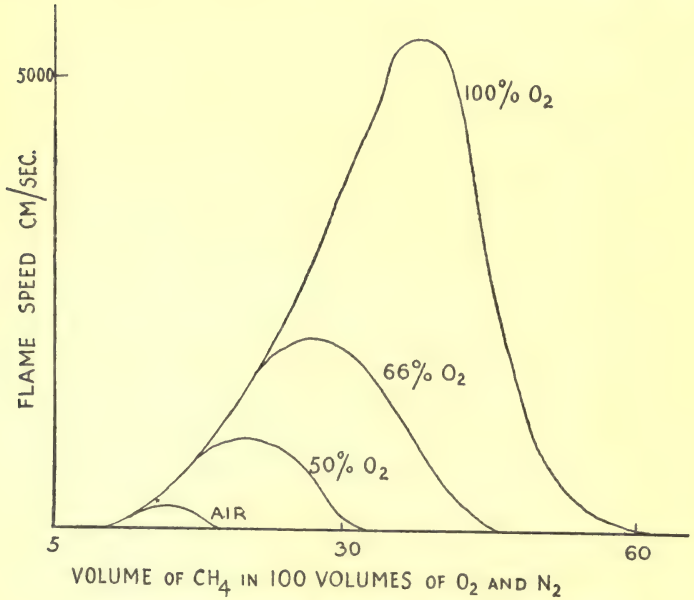


FIG. 19.—Flame Speeds of Methane in Oxygen-enriched Air (Payman).

These results may be compared, in so far as their general characteristics are concerned, with those given in Fig. 18 for the speed of flames of methane mixed with atmospheres less rich in oxygen than ordinary air.[11]

The curve showing the results for methane in pure

oxygen is interesting. The maximum flame speed is 5500 cms. per second—more than fifty times the maximum speed attained in air.

Further, the maximum speed in oxygen occurs with the mixture containing the two gases in the proportions necessary for complete combustion, namely, one volume of methane to two of oxygen. This is interesting in view of the observation that when a detonation wave is set up in mixtures of methane and oxygen, its speed is greatest when the two gases are present in equal proportions, namely, CH_4+O_2.

In the case of hydrogen and air, the measurement is less easy inasmuch as the period of uniform movement does not, in the majority of mixtures, extend over so great a distance as 1 metre. In contradistinction to mixtures of methane and air, the maximum speed of propagation of the flame does not occur with the mixture containing hydrogen and oxygen in combining proportions, namely, 29·5 per cent. of hydrogen, but with mixtures over the range 38 to 45 per cent. of hydrogen.[12]

In Fig. 20 are shown diagrammatically the relative speeds attained on firing mixtures of three saturated hydrocarbons with varying proportions of air,[13] and for the sake of ready reference, the limit and maximum flame speeds for various gases mixed with air are given in the accompanying table.

It will be observed that the limit speeds for both the lower and higher limit concentration values tend to approach the same value (approximately 20 cms. per second) for all the gases concerned.

Further, the maximum speeds of the hydrocarbon gases are practically the same, namely, about 82 cms. per second, with the sole exception of methane. The value for this last gas is about 67 cms. per second.

It is rather remarkable to note that in each instance the mixture possessing the maximum flame speed should contain more combustible gas than

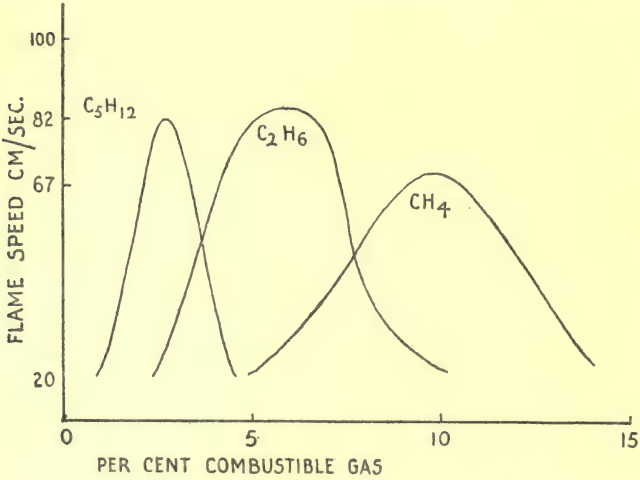


Fig. 20.—Flame Speeds of Hydrocarbon Gases (Payman).

is required for complete combustion, save again in the case of methane. The ratio

$$\frac{\text{oxygen required for complete combustion}}{\text{oxygen yielding maximum flame speed}}$$

is approximately 1 to 0·85 by volume.[14] In the case of methane, the maximum speed occurs with the proportion required for complete combustion.

Flame Propagation in Air Mixtures of Various Combustible Gases.

Gas.	Lower Limit.		Maximum Flame Speed.		Upper Limit.	
	Gas.	Flame Speed.	Gas.	Flame Speed.	Gas.	Flame Speed.
	Per cent.	(cm. sec.).	Per cent.	(cm. sec.).	Per cent.	(cm. sec.).
CH_4 . [13]	5·80	23·3	9·52	66·6	13·35	19·1
C_2H_6 . [13]	3·30	18·1	6·53	85·6	10·60	19·7
C_3H_8 . [13]	2·37	20·8	4·71	82·1	7·30	20·3
C_4H_{10} . [13]	1·95	20·1	3·66	82·6	6·53	20·3
C_5H_{12} . [13]	1·61	20·2	2·92	83·0	5·40	20·2
H_2 . . [15]	6·19	10·0	36·3 [12]	503·0 [12]	71·39	50·0
CH_4+H_2 [15]	6·03	15·0	14·93	135·3	20·80	24·3
CO . [15, 16]	16·29	19·5	44·84	60·1	71·19	19·4
CH_4+CO [15]	9·45	21·9	15·95	91·3	21·55	19·8
$CO+H_2$. [15]	9·25	18·2	45·92	315·2	71·34	44·4
C_2H_2 . [17]	3·45	41·0	8·9	282·0	16·0	68·0

Experiments with gases other than hydrocarbons, such, for example, as hydrogen and carbon monoxide, or with mixtures of these with methane, do not manifest the same regularities as the simple hydrocarbon gases.[15] This will be evident from a glance at the curves given in Fig. 21.

Although in most cases the lower limit mixtures yield flame speeds not widely removed from 20 cms. per second, in the case of hydrogen the lower limit speed is only 10 cms. Considerable variation is manifest in the upper limit speeds, that of hydrogen being 50 cms., and that of a mixture of hydrogen and carbon monoxide in equal proportions by volume being 44·4 cms. per second. (See Table.)

The most pronounced speed variation, however, occurs with the various maxima. Thus, the maximum speed attained in a mixture of hydrogen and air is nearly eight times the maximum attained in methane and air.[18]

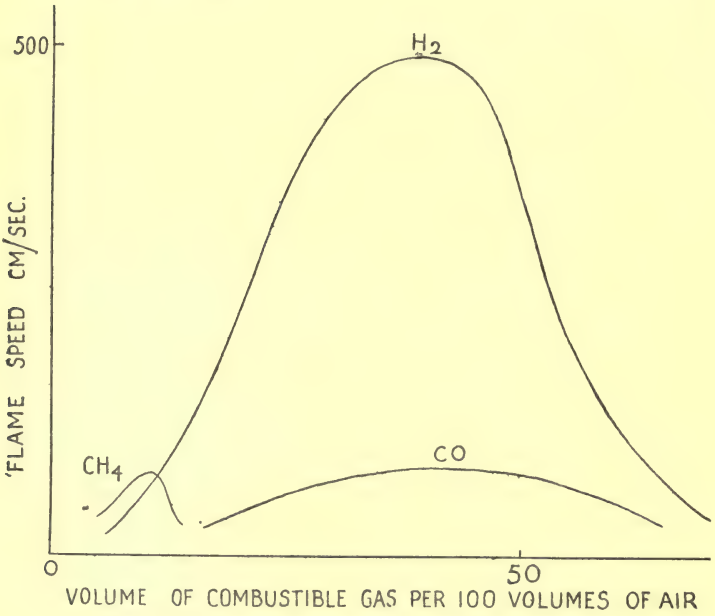


Fig. 21.—Flame Speeds with H_2 and CO (Payman).

B. Gaseous Explosions.

A gaseous **explosion** may be defined as a reaction between two or more gases which proceeds with rise of temperature and an ever-increasing velocity, until a maximum high velocity is attained, when it becomes practically constant.

There is thus no strict line of demarcation between an explosion and the uniform slow propagation of flame which was considered in the previous section. It is purely a question of relative velocities.

It was not until 1880 that the attention of scientists generally was directed to the fact that practically nothing was known of the velocity with which explosion waves could travel in gases. In that year a coal-gas explosion occurred in Tottenham Court Road, and it was concluded from the evidence

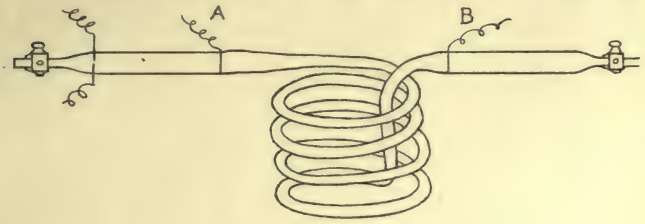


Fig. 22.—Dixon's Apparatus.

that the wave must have travelled with a velocity of at least 100 yards per second. During the next two years two important researches were published on the subject, one by Mallard and Le Chatelier [19] in 1881, and the second by Berthelot and Vieille [20] in 1882. These were followed by the classical research of Dixon [21] in 1893.

The apparatus used by Dixon in his experiments with hydrogen and oxygen and other inert gases is shown diagrammatically in Fig. 22, and consisted of a coil of lead piping some 75 metres in length which could easily be placed in a tank of water and kept at any desired uniform temperature. Each

free end was connected with a horizontal tube, the one fitted with a pair of platinum wires for sparking, and both containing strips of silver-foil, A and B. On passage of a spark, the explosion wave ruptured A, passed through the lead coil, and on emerging at B ruptured the second strip. The time-intervals between the ruptures at A and B were measured electrically and thus gave the velocity of the explosion wave. In his experiments with chlorine and hydrogen, Dixon employed straight pipes of wrought iron, glass lined. The silver membranes were coated with paraffin wax to prevent chemical action.

As the result of these researches the following facts have been experimentally established :—

(1) The velocity of explosion is independent of the material of which the tube is made, provided the diameter is above a certain minimum. This is precisely what was found in the experimental study of the uniform slow propagation of flame.

(2) The velocity of explosion is independent of the diameter of the tube above a certain small limit. If only 3 mm. in diameter no explosion will pass (Davy), but the rate is the same in a tube of 5 mm. diameter as in one of 15 mm.

(3) The explosion wave increases rapidly in velocity from the moment of its inception until a high maximum velocity is attained, after which its rate of propagation is uniform.

This velocity is very high, being several times that of sound. In the case of hydrogen and oxygen in the proportions H_2+O, the velocity found by Berthelot was 2810 metres, and by Dixon 2821 metres per second at room temperature—results showing a remarkably close agreement.

(4) Increase of pressure was found by Dixon [22] to increase the velocity of explosion, although when once a certain maximum pressure has been reached, further increase does not appear to appreciably alter the velocity.

Influence of Pressure on the Explosion Velocity (Dixon).

Gases.	Velocity of Explosion Wave at 10° C. in Metres per Second.	Pressure mm.
H_2+O	2627	200
...	2775	500
...	2821	760
...	2856	1100
...	2872	1500

(5) Rise of temperature tends to reduce the velocity. This is evident from the following data [21]:—

Gases.	Velocity of Explosion Wave at (Metres per Second):	
	10° C.	100° C.
H_2+O	2821	2790
$C_2H_4+2O_2$	2581	2538
$C_2N_2+O_2$	2728	2711

(6) The presence of inert gases may lead either to the acceleration or retardation of the velocity of the explosion wave. If one of the combustible gases is in great excess, it behaves like an inert gas of similar volume and density. This is well illustrated by the following results in the case of oxygen[21]:—

Gaseous Mixture.	Velocity of Explosion.	Gaseous Mixture.	Velocity of Explosion.
H_2+O	2821	H_2+O	2821
H_2+O+3O	1927	H_2+O+3N	2055
H_2+O+5O	1707	H_2+O+5N	1822
H_2+O+7O	1281	H_2+O+7N	none

On the other hand, hydrogen, on account of its low density, accelerates the velocity unless present in very great excess.

(7) An explosion wave is characterised by incompleteness of combustion.[21] Even electrolytic gas does not wholly combine under these conditions. In the case of moist $CO+O$, there is a similar residuum of unburned gas, but no hydrogen peroxide has been detected as would be expected if Traube's theory (see p. 45) were correct.

(8) Water vapour exerts an important influence upon the velocity of explosion of carbon monoxide and oxygen.[21] Up to 35° C. the water vapour in the saturated gases assists

the explosion, but above that temperature it begins to act as an inert gas, reducing the velocity. Thus :—

Condition of CO+O.	Per cent. Water Vapour.	Velocity in Metres per Second.
Well dried . .	nil	1264
Saturated at 10° C.	1·2	1676
,, ,, 35° C.	5·6	1738
,, ,, 75° C.	38·4	1266

Pressure developed during an Explosion.—This is a problem of great importance to engineers, more particularly in connection with internal combustion engines.[23] The earliest measurements were made by Bunsen[24] who, by means of a lever, determined the weight that must be placed upon a movable lid resting on a cylinder, to prevent its being forced off during an explosion of gases within the cylinder. He found as follows :—

	Pressure generated.
CO + O . . .	10·1 atmospheres
H_2 + O . . .	9·5 ,,

Berthelot and Vieille[20] obtained closely similar results.

The various methods now in use consist essentially in exploding gaseous mixtures in metallic cylinders and automatically recording the pressures exerted. The pressures obtained in practice are never equal to those to be expected from theoretical considerations, neither are the temperatures. There are several

contributory causes, chief amongst which may be cited :—

(*a*) Dissociation of the gaseous products.
(*b*) Incomplete combustion.
(*c*) Variation in specific heats of gases under the special conditions, which render the theoretical calculations uncertain.

SECTION IX.

Surface Combustion.

If a piece of platinum wire or platinised asbestos after being warmed in a Bunsen flame is, whilst still warm, plunged into a stream of coal-gas and air issuing from a Bunsen burner, the whole begins to glow. The coal-gas is uniting with the oxygen of the air on the surface of the platinum, evolving sufficient heat to raise the metal to incandescence, but usually without the production of flame. If the coal-gas is replaced by hydrogen, the platinum or platinised asbestos becomes sufficiently hot to heat the gas up to its ignition temperature, with the result that the hydrogen bursts into flame (see p. 48). This was first demonstrated by Davy[1] in 1818, who employed a spiral of platinum wire.

An effective lecture experiment illustrating surface combustion consists in inserting a short platinum spiral attached to a glass rod, and gently warmed, into a beaker containing a few c.c. of methyl alcohol. The mouth of the beaker is now loosely covered with a piece of filter-paper, which prevents flames

from rising, and platinum glows brightly as the alcohol burns upon its surface (see Fig. 23).

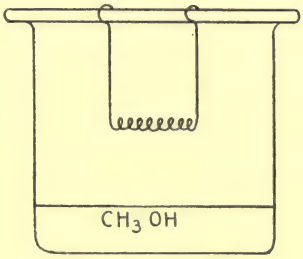


Fig. 23.

This experiment is merely a modification of a well-known method of preparing formaldehyde, which consists in passing a mixture of air and methyl alcohol vapour over a heated platinum wire.[2] The reaction is usually represented by the equation

$$CH_3OH = \underset{\text{Formaldehyde}}{HCHO} + H_2.$$

This is followed by a certain amount of further dehydrogenation[3]

$$HCHO = H_2 + CO$$

and subsequent oxidation, which may be more or less complete according to circumstances. Thus:

$$H_2 + CO + O_2 = H_2O + CO_2.$$

The reaction, when once started, is self-supporting and lamps have been constructed for this purpose.[4]

A pretty variation of this experiment for popular demonstration, consists in suspending by means of

a copper wire a star-shaped piece of platinum-foil from a glass support in a tumbler or other suitable glass vessel, containing some perfumed alcohol. The platinum is first warmed and then lowered into the vapour, and when it has become red hot, and flames are escaping from the vessel, a metal lid, pierced with several holes for ventilation, placed on top. This extinguishes the flames, but the platinum star continues to glow. If the room is darkened the effect is very beautiful.

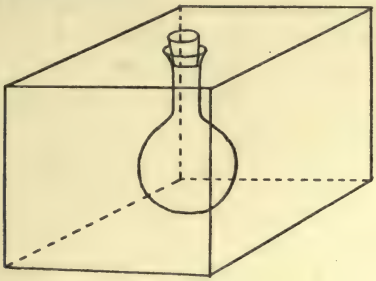


Fig. 24.

Electrolytic gas, that is, a mixture of two volumes of hydrogen with one of oxygen, may similarly be fired by contact with a platinum spiral[5] warmed to 50° C. Platinum black is particularly active in this respect,[6] and if a small quantity is introduced into a mixture of electrolytic gas a violent explosion occurs as the gases unite to form water.

This may be demonstrated in a convenient manner by inserting a flask filled with electrolytic gas into a heavy upturned wooden box, the mouth of the flask just appearing through a small hole in the bottom of the box as shown in Fig. 24. The cork

is now removed and a trace of platinum black added. The flask may be blown to pieces by the force of the explosion, the fragments of glass falling harmlessly down.

Combustions of this kind are intimately associated with and affected by the surface conditions of the catalyser, and are therefore referred to under the general title of **surface combustion.**

The phenomena attending this type of combustion have been carefully studied by numerous investigators, and the correctness of the following generalisations appears now to have been established—

1. *The property of accelerating gaseous combustion at temperatures below the ignition-point is shared by all substances irrespective of their chemical composition.* That it is not the peculiar and exclusive property of the platinum metals, nor indeed of metals in general, was demonstrated many years ago. Thus, for example, in 1887 Fletcher[7] showed that Davy's experiment may be varied by allowing a mixture of air and coal-gas to impinge upon a large ball of iron wire, previously warmed to the necessary temperature to induce surface combustion. The gas and oxygen readily unite under these conditions, and the temperature rises rapidly, the iron being raised to incandescence.

Dulong and Thénard[8] in 1823 found that finely divided silver causes the combustion of hydrogen in oxygen at 150° C., thin gold leaves at 260° C., and even fragments of non-metallic bodies such as charcoal, pumice, porcelain, quartz, and glass at temperatures below 350° C. Curiously enough, angular pieces of

glass were found to be more efficient than glass balls of equal superficial area.

2. A second interesting feature of surface combustion lies in the observation that whilst at lower temperatures there exist very marked differences in the catalysing powers of various solids, at high temperatures not only are all catalysing powers enhanced, but the aforesaid chemical differences tend to disappear. At bright incandescence all solids apparently behave pretty much alike.

The Combustion of Electrolytic Gas.

The combustion of electrolytic gas under varying conditions of temperature and catalysis has been made the subject of considerable investigation.

Although in the course of several months a mixture of hydrogen and oxygen when moist and exposed to daylight shows signs of chemical combination,[9] the action is inappreciable during the course of an ordinary experiment. Indeed, electrolytic gas has been maintained at temperatures as high as 400° C. for a week without showing any appreciable combination[10] in the absence of a catalyst other than moisture.

For a most thorough and exhaustive study of the combustion of mixtures of hydrogen and oxygen at slightly higher temperatures in contact with various catalysing surfaces, we are indebted to Bone and Wheeler.[11]

Their apparatus consisted essentially of a closed system in which the mixed gases could be con-

tinuously circulated through a Jena hard glass combustion tube containing the surface under examination, and maintained at any desired temperature in a gas furnace. The gases, measuring *in toto* about 1500 c.c., were kept in circulation by means of a mercury pump, any fall in pressure being readily measured. Arrangements were made also for removing samples of the gas whenever necessary, in order to check the pressure records without in any way interfering with the course of the reaction. The electrolytic gas employed in the research was prepared by the electrolysis of an aqueous solution of barium hydroxide, thereby ensuring its freedom from ozone, hydrogen peroxide, or any hydrocarbon impurity.[9] The same method was adopted also for the preparation of hydrogen alone, whilst if oxygen was required it was obtained by heating potassium permanganate.

As catalysts the following types of substances were employed:—

(*a*) Refractory acidic oxide—porcelain.
(*b*) Refractory basic oxide—magnesite.
(*c*) Easily reducible oxides—oxides of nickel, iron, and copper.
(*d*) Metals—silver, gold, platinum, and nickel.

Porous Porcelain.—In the first series of experiments the combustion tube was closely packed with fragments of unglazed porcelain which had previously been heated to 1000° C. It was perfectly white in colour and contained only 0·05 per cent. of ferric oxide. Electrolytic gas was circulated through the

tube which was maintained at 450° C., and the rate of combination of the hydrogen and oxygen determined. According to the equation

$$2H_2 + O_2 = 2H_2O$$

a reaction of the third order might be anticipated in accordance with the Law of Mass Action, and indeed this is precisely what Bodenstein [12] believed his experiments sufficed to establish. Bone and Wheeler, however, have shown that this is incorrect. The reaction is purely a surface phenomenon, *the rate of combination being directly proportional to the pressure of the dry gas.* This is clearly demonstrated by the following table of results obtained at 450° C., C_0 representing the initial pressure of the gases, and C_t that at time t.

Time (Hours).	Pressure of Electrolytic Gas. mm.	$k_1 = \frac{1}{t} \log \frac{C_0}{C_t}$.
0	465·6	...
36	163·9	0·0126
48	116·1	0·0125
60	84·6	0·0123
72	60·7	0·0123
84	42·9	0·0123
96	28·6	0·0126
108	20·6	0·0125
120	14·6	0·0125

The reaction is thus seen to be one of the first order.

The experiments were varied by mixing electrolytic gas with free hydrogen or oxygen, so that the reacting mixture contained an excess of one

of the constituents above that required for the reaction

$$2H_2 + O_2 = 2H_2O.$$

It was then found that the rate of reaction of the gases was mainly if not entirely *proportional to the partial pressure of the hydrogen.* This result was hardly to be expected from a consideration of the laws of diffusion. Since the rate of diffusion of hydrogen is four times that of oxygen it follows that, assuming the rate of combination at the surface to be very great, there would always be an excess of hydrogen at the surface when ordinary electrolytic gas is employed, the rate of combination being determined by the rate of diffusion of the oxygen. Addition of oxygen to the system to an amount corresponding to the proportion $2H_2+4O_2$ should therefore increase the rate of combustion to a maximum, whilst any further addition either of oxygen or hydrogen would reduce it. The fact, however, that this is not the case suggests that the reaction is indirect and complicated, and this is supported by the observation that the catalysing power of porcelain is appreciably enhanced by exposure to hydrogen prior to the introduction of electrolytic gas. This is not due to chemical reduction of the porcelain, as otherwise the effect would be increased by prolonged exposure to hydrogen at high temperatures—which it is not. Furthermore, the occluded hydrogen can always be completely removed by pumping when the porcelain is at red heat, although the gas is obstinately retained at the ordinary temperature.

Previous exposure to oxygen does not appear to stimulate the catalytic activity of porcelain towards electrolytic gas. The conclusion is therefore drawn —to quote the authors' own words—that:

"Porous porcelain occludes, or condenses, both hydrogen and oxygen at rates which depend to some extent upon the physical condition and past history of the surface. In general, however, whereas in the case of oxygen the process is extremely rapid and the surface layer is soon saturated, the occlusion of hydrogen is slower and the limit of saturation much higher. Combination between the occluded gases occurs at a rate either comparable with, or somewhat faster than, the rate at which the film of occluded oxygen is renewed, but considerably faster than the rate of occlusion of hydrogen."

Experiments with **magnesite** at 430° C. led to precisely similar conclusions. The results of the experiments with **silver** are particularly interesting for two reasons:

(*a*) The oxides of silver are unstable above 350° C.[13]

(*b*) Analogy with sodium and copper,[14] two elements belonging to the same vertical column of the Periodic Table, suggests the possibility that silver may form a hydride at elevated temperatures.

It was found, as with porcelain, that the rate of combination of hydrogen and oxygen in electrolytic gas in contact with pure silver gauze is directly proportional to the pressure. Hydrogen exerts a marked stimulating effect.

During the course of the experiments the surface of the silver became "frosted" when heated to near its melting-point,[15] and its catalytic activity increased some threefold, but was reduced again by rubbing down the surface. The behaviour of the surface suggests the formation of a hydride and not mere occlusion or condensation such as occurs with porcelain.

Gold at 250° C. showed acceleration with hydrogen, but a microscopic examination of the gauze revealed no sign of disintegration or of hydride formation. The catalytic action would thus appear to be merely an example of superficial occlusion or condensation. In the presence of ferric oxide and of nickel oxide electrolytic gas combines rapidly without producing any change in the catalysing surface.

Copper oxide behaves in an exceptional manner. Not only is its action slow, but the rate of formation of water is proportional to the partial pressure of the oxygen when pure electrolytic gas is not employed.

This is explained on the assumption that a film of "active" oxygen condenses on its surface, thereby protecting the catalysing oxide from the hydrogen that would otherwise reduce it. At low pressures this film becomes too attenuated to ensure complete protection, with the result that steam is formed by the hydrogen penetrating through to the oxide and reducing it.

An interesting industrial application of surface combustion has been devised by Bone[16] and consists in heating a porous firebrick diaphragm, AB (Fig. 25), by passing a current of coal-gas through C into the

feed chamber D and igniting it on the outer surface of the diaphragm as it percolates through. An increasing supply of air, under slight pressure to prevent "striking back," is now added to the gas entering at C until the requisite amount has been reached. The flame outside AB becomes non-luminous, diminishes in size, and finally retreats on to the surface of the diaphragm, the whole surface layer of which eventually becomes red hot.

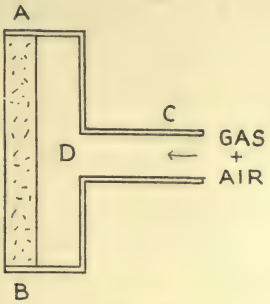


Fig. 25.

There are several interesting features attendant upon this type of combustion. For example, the heat is confined to a thin layer of the diaphragm, usually less than 0·25 in. in thickness, the back of the diaphragm remaining quite cool. The combustion of the gases is practically perfect and is independent of the external air provided the gas entering at C is fully aerated; indeed the combustion will proceed with unimpaired incandescence even in an atmosphere of carbon dioxide.

Selective Combustion.—A useful field for investigation would appear to lie in the possibility of

various catalysing substances effecting selective combustions in mixtures of combustible gases. For example, it has been shown [17] that small quantities of carbon monoxide in hydrogen can be preferentially oxidised to carbon dioxide by passing the gaseous mixture admixed with a small quantity of oxygen over certain catalysts. The subject has been but little studied.

BIBLIOGRAPHY AND NOTES.

(The Abbreviations used are substantially the same as those adopted by the Chemical Society.)

Section I.

[1] Using the older data of Thomsen. These figures have been revised by Mixter, Amer. J. Sci., 1903, **16**, 214.

[1a] A pretty experiment illustrating chlorine burning in hydrogen and hydrogen in air is described by Egerton, Chem. News, 1912, **105**, 232.

[2] H. B. Baker (Trans. Chem. Soc., 1902, **81**, 400) has confirmed this by showing that the moist gases unite slowly in sunlight, whilst the dried gases do not. After four months his electrolytic gas had contracted by 4·35 per cent.

[3] Meyer and Raum, Ber., 1895, **28**, 2804.

[4] Bone and Wheeler, Phil. Trans., 1906, A, **206**, 1.

[5] See Smithells, British Assoc. Reports, 1907.

Section II.

[1] For an interesting and detailed account of the origin, development, and final overthrow of the theory of phlogiston the reader is referred to Freund, The Study of Chemical Composition (C. U. Press, 1904), Chapter I.

[2] This remarkable disappearance of the phlogiston during calcination had not escaped the notice of Scheele (1742-1786), who evidently realised the anomaly. (See Chemical Treatise on Air and Fire, 1777. Alembic Club Reprints, No. 8.)

[3] Priestley, Experiments and Observations on Different Kinds of Air, 1774, ii., 28. Alembic Club Reprints, No. 7. Scheele had already discovered oxygen in 1771, but withheld publication for several years, so that Priestley's discovery was the first to be publicly announced. See Crell's Annalen, 1785, **2**, 229, 291.

Section III.

[1] This theory was vigorously supported by Lang (Zeitsch. physikal. Chem., 1888, **2**, 161), who claimed to have proved that, in the combustion of carbon, the formation of dioxide precedes that of the monoxide. His conclusions, however, were disputed by Dixon (Trans. Chem. Soc., 1899, **75**, 630).

[2] C. J. Baker, Trans. Chem. Soc., 1887, **51**, 249.

[3] H. B. Baker, Proc. Roy. Soc., 1888, **45**, 1; Phil. Trans., 1888, **179**, A, 571.

[4] Rhead and Wheeler, Trans. Chem. Soc., 1912, **101**, 846; 1913, **103**, 461, 1210.

[5] Above 900° C. it appears probable that reduction in pressure can by itself effect the removal of the oxides.

[6] See Dewar, Chem. News, 1908, **97**, 16; Redgrove, *ibid.*, p. 36; Aschan, Chem. Zeit., 1909, **33**, 561; Dunroth and Kerkovius, Annalen, 1913, **399**, 120. Contrast, however, Hans Meyer, Monatsh., 1914, **35**, 163.

[7] But see Rhead and Wheeler, Trans. Chem. Soc., 1913, **103**, 1210.

Section IV.

[1] Smithells, J. Soc. Chem. Ind., 1891, **10**, 994; Vivian B. Lewes, *ibid.*, 1892, **11**, 231.

[2] See Sketches from the Life of Sir Edward Frankland (Spottiswoode, 1902), pp. 234-56.

[2a] See Senftleben and Benedict (Kolloid. Zeitsch., 1920, **26**, 97), who show that a candle flame behaves towards a beam of light in a similar manner to a turbid medium.

[3] See, for example, Fery, Compt. rend., 1903, **137**, 909 ; Lewes, J. Soc. Chem. Ind., 1892, **11**, 231.

[4] Smithells and Ingle, Trans. Chem. Soc., 1892, **61**, 204; Smithells and Dent, *ibid.*, 1894, **65**, 603.

[5] Lewes, *loc. cit.*

[6] On dismantling the experiment, put your finger at B to extinguish the flame at C. Then cut off the gas. The gauze at A will prevent the flame from "striking back."

Section V.

[1] Dixon, Cantor Lectures, 1884.

[2] Dalton, A New System of Chemical Philosophy, 1808, vol. i.

[3] Kersten, J. prakt. Chem., 1861, **84**, 310.

[4] See also Misteli, J. Gasbeleuchtung, 1905, **48**, 802.

[5] Bone and Wheeler, Trans. Chem. Soc., 1902, **81**, 535.

[6] Bone and Wheeler, *ibid.*, 1903, **83**, 1074.

[7] Bone and H. L. Smith, *ibid.*, 1905, **87**, 910.

[8] Losanitsch and Govitschitsch, Ber., 1897, **30**, 136; de Hemptinne, Bull. Acad. Roy. Belg., 1897, **34**, 269 ; Solvay and Slosse, *ibid.*, 1898, **35**, 547.

[9] Armstrong, Trans. Chem. Soc., 1903, **83**, 1088.

[10] Bone and Drugman, *ibid.*, 1906, **89**, 679.

[11] Bone, British Assoc. Reports, 1910, p. 491 ; Bone and Stockings, Trans. Chem. Soc., 1904, **85**, 693.

[12] Bone and Drugman, Proc. Chem. Soc., 1904, **20**, 127 ; Drugman, Trans. Chem. Soc., 1906, **89**, 939.

[13] Bone and Stockings, *loc. cit.*

[14] Bone and H. L. Smith, Trans. Chem. Soc., 1905, **87**, 910.

[15] Bone, British Assoc. Reports, 1910, p. 491 ; Bone and Wheeler, Trans. Chem. Soc., 1904, **85**, 1637.

[16] Bone, British Assoc. Reports, 1910, p. 491 ; Bone and Andrew, Trans. Chem. Soc., 1905, **87**, 1232.

[17] Dixon, British Assoc. Reports, 1880, p. 503 ; Chem. News, 1882, **46**, 151 ; Phil. Trans., 1884, **175**, 630 ; Trans. Chem. Soc., 1886, **49**, 95.

[18] Traube, Ber., 1882, **15**, 666.

[19] Traube's line of argument appears weak.

[20] Constam and Hansen, Zeitsch. Elektrochem., 1896, **3**, 137, 445; Bach, Compt. rend., 1897, **124**, 2, 951.

[21] Durrant, Chem. News, 1896, **73**, 228; 1897, **75**, 43; Proc. Chem. Soc., 1896, **12**, 244.

[22] Smithells and Dent, Trans. Chem. Soc., 1894, **65**, 603.

[23] Baker, Trans. Chem. Soc., 1902, **81**, 400.

[24] Bone and Haward, Proc. Roy. Soc., 1921, A, **100**, 67.

Section VI.

[1] This illustration is borrowed from Smithells, British Assoc. Reports, 1907.

[2] For example, a mixture of air and vapour of carbon bisulphide issuing into an atmosphere of nitrogen.

[3] Davy, Phil. Trans., 1816, p. 7.

[4] Krause and V. Meyer, Annalen, 1891, **264**, 85; Askenasy and V. Meyer, Annalen, 1892, **269**, 49; Meyer and Raum, Ber., 1895, **28**, 2804; Bone and Wheeler, Trans. Chem. Soc., 1902, **81**, 535; Emich, Monatsh., 1900, **21**, 1061.

[5] Mallard and Le Chatelier, Compt. rend., 1880, **91**, 825; Meyer and Freyer, Ber., 1892, **25**, 622; Zeitsch. physikal. Chem., 1893, **11**, 28; Meyer and Münch, Ber., 1893, **26**, 2421; Gautier and Hélier, Compt. rend., 1896, **122**, 566; Hélier, Ann. Chim. Phys., 1897, (7), **10**, 521; Bodenstein, Zeitsch. physikal. Chem., 1899, **29**, 665.

[6] See Dixon and Coward, Trans. Chem. Soc., 1909, **95**, 514.

[7] Falk, J. Amer. Chem. Soc., 1906, **28**, 1517; 1907, **29**, 1536; Dixon and Crofts, Trans. Chem. Soc., 1914, **105**, 2036.

[8] This apparatus, so beautifully simple in theory, required a vast amount of manipulative skill and ingenuity to bring to perfection in practice. The student is strongly recommended to study the details as given in the original paper (Reference 7).

[9] M'David, Trans. Chem. Soc., 1917, **111**, 1003.

[10] White and Price (*ibid.*, 1919, **115**, 1248) conclude, as the result of their experiments, that this method cannot give the true ignition temperature and is "not strictly trustworthy even for comparative purposes."

[11] Data for coals, peat, etc., are given by Holm, Zeitsch. angew. Chem., 1913, **26**, 273.

[12] M'Crea and Wilson, Chem. News, 1907, **96**, 25. See résumé by Hill, *ibid.*, 1907, **95**, 169.

[13] This depends partly on the composition of the gas and partly also on the manner in which the platinised asbestos is made.

Section VII.

[1] Davy, Collected Works, vi., p. 24.

[2] Burgess and Wheeler, Trans. Chem. Soc., 1911, **99**, 2013.

[3] Burgess and Wheeler, *loc. cit.*, p. 2024.

[4] Burgess and Wheeler, *ibid.*, 1914, **105**, 2591.

[5] Terres and Plenz, J. Gasbeleuchtung, 1914, **57**, 990, 1001, 1016, 1025. Confirmed by Mason and Wheeler, Trans. Chem. Soc., 1918, **113**, 45, whose data are given in the table.

[6] Taffanel, Compt. rend., 1913, **157**, 593. See also Burrell and Robertson, U.S. Bureau of Mines, Technical Paper No. 121, 1916; Mason and Wheeler, *loc. cit.*

[7] Wheeler and Whitaker, Trans. Chem. Soc., 1917, **111**, 267.

[8] Given by Burgess and Wheeler, *ibid.*, 1911, **99**, 2013.

[9] Le Chatelier, Leçons sur le Carbone, p. 266.

[10] Clowes, Proc. Roy. Soc., 1894, **56**, 2; 1895, **57**, 353.

[11] Müller, Chem. Zentr., 1917, i., 991.

[12] Dollwig, Kolls, and Loevenha, J. Amer. Chem. Soc., 1917, **39**, 2224.

Section VIII.

[1] Mallard and Le Chatelier, Recherches (Paris, 1883).

[2] Mason and Wheeler, Trans. Chem. Soc., 1917, **111**, 1044.

[3] Wheeler, Trans. Chem. Soc., 1914, **105**, 2606.

[4] Payman and Wheeler, *ibid.*, 1919, **115**, 36.

[5] Mason and Wheeler, *ibid.*, 1917, **111**, 1044.

[6] Parker and Rhead (*ibid.*, 1914, **105**, 2150) employed thin strips of Wood's alloy, melting at 72° C.

[7] Mallard and Le Chatelier, Ann. Mines, 1883, (8), **4**, 312; Haward and Sastry, Trans. Chem. Soc., 1917, **111**, 841; Mason and Wheeler, *ibid.*, 1919, **115**, 578.

[8] Parker, *ibid.*, 1915, **107**, 328; Mason and Wheeler, *ibid.*, 1917, **111**, 1044.

[9] Mason and Wheeler, *ibid.*, 1917, **111**, 1044; Burgess and Wheeler, *ibid.*, 1914, **105**, 2596; Payman, *ibid.*, 1919, **115**, 1436.

[10] Payman, *ibid.*, 1920, **117**, 48.

[10a] Parker, *ibid.*, 1914, **105**, 1002.

[11] Numerically the results are not strictly comparable, inasmuch as the former were obtained with tubes 5 cms. in diameter, whilst the latter were obtained with tubes of 2·5 cms. diameter.

[12] Haward and Otagawa, Trans. Chem. Soc., 1916, **109**, 83.

[13] Payman, *ibid.*, 1919, **115**, 1446.

[14] Calculated from the data given by Payman (Reference 13, p. 1448).

[15] Payman, Trans. Chem. Soc., 1919, **115**, 1454.

[16] Saturated with moisture; temperature 12° C. Pressure 75·0 cms.

[17] Mason and Wheeler, Trans. Chem. Soc., 1919, **115**, 578.

[18] A few experiments have recently been carried out on the vertical propagation of flame. See Mason and Wheeler, *ibid.*, 1920, **117**, 1227.

[19] Mallard and Le Chatelier, Compt. rend., 1881, **93**, 148.

[20] Berthelot and Vieille, *ibid.*, 1882, **94**, 101; 1882, **95**, 151, 199; Berthelot, *ibid.*, 1882, **94**, 149.

[21] Dixon, Phil. Trans., 1893, **184**, 97.

[22] Berthelot believed that alteration in pressure made no appreciable difference in the velocity.

[23] See Clerk, Gas, Petrol, and Oil Engine (Longmans, 1909), vol. i.

[24] Bunsen, Gasometrische Methoden (Braunschweig, 1877).

Section IX.

[1] Davy, Phil. Trans., 1817, **107**, 77; Quart. J. Sci., 1818, **5**, 128.

[2] Hofmann, Annalen, 1868, **145**, 357; Ber., 1869, **2**, 152; 1878, **11**, 1686.

[3] Thomas, J. Amer. Chem. Soc., 1920, **42**, 867.

[4] Tollens, Ber., 1895, **28**, 261.

[5] Erman, Abhandl. Akad. Wiss. Berlin, 1818-19, p. 368.

[6] Doebereiner, Schweigger's J., 1823, **34**, 91; **38**, 321; **39**, 159; **42**, 60; **63**, 465.

[7] Fletcher, J. Gas Lighting, 1887, **1**, 168.

[8] Dulong and Thénard, Ann. Chim. Phys., 1823, **23**, 440; 1823, **24**, 380.

[9] Baker, Trans. Chem. Soc., 1902, **81**, 400.

[10] Bone and Wheeler, *ibid.*, 1903, **83**, 548. Compare also Meyer and Raum, Ber., 1895, **28**, 2804; Gautier and Hélier, Compt. rend., 1896, **122**, 566.

[11] Bone and Wheeler, Phil. Trans., 1906, A, **206**, 1.

[12] Bodenstein, Zeitsch. physikal. Chem., 1899, **29**, 665.

[13] Carnelley and Walker, Trans. Chem. Soc., 1888, **53**, 79.

[14] Leduc, Compt. rend., 1902, **135**, 1332; 1903, **136**, 1254.

[15] Graham had made a somewhat similar observation on heating silver wire to redness and cooling in hydrogen (Phil. Trans., 1866, **156**, 435).

[16] Bone, J. Roy. Soc. Arts, 1914, **62**, 787, 801, 818; Coal and its Scientific Uses (Longmans, 1918).

[17] Rideal, Analyst, 1919, **44**, 89; Trans. Chem. Soc., 1919, **115**, 993.

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